1,3 dipolar cycloaddition product **21**: mp 87–88°; ir 1615, 775 cm^{-1} (N–O); λ_{max}^{EtOH} 245, 293 mμ; nmr (in CCl_4 with external TMS) δ 1.1 (t, 6 H), 3.2 (q, 4 H), 7.23 (m, 10 H).

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.15; H, 6.90; N, 9.59. Found: C, 77.93; H, 6.87; N, 9.35.

Reaction of N,N-Diethylphenylethynylamine with Tetraphenylcyclopentadienone.—Tetraphenylcyclopentadienone, 0.5 g (1.5 mmol), and the ynamine, 0.25 g (1.5 mmol), in 3 ml of dry diglyme were heated in a sealed tube at 180° for 12 hr. Filtration of the mixture and recrystallization of the solid from toluene gave 50 mg (7% yield) of pentaphenyl-N,N-diethylaniline (**22**): mp 326–328; nmr (in $CDCl_3$ with internal TMS) δ 0.55 (t, 6 H), 2.5 (q, 4 H), 6.80 (m, 15 H), 7.10 (10 H).

Anal. Calcd for $C_{40}H_{35}N$: C, 90.69; H, 6.66; N, 2.64. Found: C, 90.90; H, 6.55; N, 2.90.

2-Naphthal- and 3-Pyridalsulfonimides.—The 2-naphthal-*p*-toluenesulfonimide was prepared in 90% yield according to the method of Kresze.[14] This sulfonimide was recrystallized from ethyl acetate and had mp 114–115°.

Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.89; H, 4.89; N, 4.53; S, 10.34. Found: C, 69.69; H, 5.04; N, 4.57; S, 10.33.

The 3-pyridal-*p*-toluenesulfonimide was prepared in the same manner in 40% yield and had mp 131–132° after recrystallization from ethyl acetate–petroleum ether (bp 30–60°).

Anal. Calcd for $C_{18}H_{12}N_2O_2S$: C, 59.99; H, 4.65; N, 10.77; S, 12.29. Found: C, 59.53; H, 4.78; N, 10.30; S, 11.99.

Registry No.—**1**, 17691-74-6; **2**, 17691-75-7; **3a**, 17691-76-8; **3b**, 17691-77-9; **3c**, 17691-78-0; **3d**, 17691-79-1; **4a**, 17691-80-4; **4b**, 17691-81-5; **4c**, 17691-82-6; **5a**, 17692-75-0; **5b**, 17692-86-3; **5c**, 17692-87-4; **5d**, 17692-88-5; **5e**, 17692-76-1; **5f**, 17693-46-8; **5g**, 17693-47-9; **5h**, 17693-48-0; **5i**, 17693-49-1; **6**, 17693-50-4; **7**, 17692-77-2; **7** HBr, 17692-78-3; **8**, 17691-83-7; **9a**, 17691-84-8; **9b**, 17691-85-9; **9c**, 17691-86-0; **9d**, 17691-87-1; **10a**, 17691-88-2; **10b**, 17691-89-3; **11a**, 17691-90-6; **11b**, 17691-91-7; **11c**, 17691-92-8; **11d**, 17691-93-9; **11e**, 17691-94-0; **12a**, 17691-95-1; **12b**, 17691-96-2; **13a**, 17691-97-3; **13b**, 17691-98-4; **13c**, 17691-99-5; **13d**, 17692-00-1; **14a**, 17692-01-2; **14b**, 17692-02-3; **15a**, 612-58-8; **15b**, 17692-04-5; **15b** picrate, 17692-05-6; **16a**, 17692-06-7; **16a** perchlorate, 17692-07-8; **16b**, 17692-08-9; **17** perchlorate, 17692-09-0; **18a**, 17692-10-3; **18b**, 17692-11-4; **18c**, 17692-12-5; **19**, 17692-79-4; **20** HBr, 17692-80-7; **21**, 17692-81-8; **22**, 17692-82-9; 3-pentyl-4-N,N-dipropylaminoquinoline, 17692-83-0; 3-pentyl-4-N,N-dipropylaminoquinoline HBr, 17743-99-6; 2-naphthal *p*-toluenesulfonimide, 17692-84-1; 3-pyridal *p*-toluenesulfonimide, 17692-85-2; **15a**, picrate, 17693-31-1.

Formation of Pyrazoles from 3,3-Disubstituted 2,4-Pentanediones. Evidence of a Novel Claisen–Cope Type of Rearrangement

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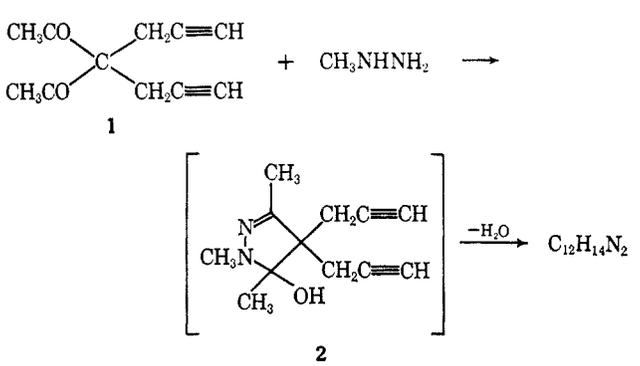
Reaction of monosubstituted hydrazines with 3,3-disubstituted 2,4-pentanediones having one or more allylic or propargylic groups at C-3 afforded high yields of pyrazoles bearing, respectively, 5-$CH_2CH(R)CH{=}CH_2$ or 5-$CH_2C(R){=}C{=}CH_2$ substituents. All evidence points to formation of an intermediate 5-methylene pyrazoline whose allylic or propargylic groups undergo a novel type of Claisen–Cope rearrangement, becoming attached to the enaminic methylene group with synchronous pyrazole formation. Treatment of 3-allyl-3-(2-propynyl)-2,4-pentanedione (**17**) with methylhydrazine leads to condensation and propargyl → allene rearrangement even at 0° and the relative rearrangement rates of allyl to propargyl were about 1.6:1 under the conditions studied. Similar reaction of methylhydrazine with 3-benzyl-3-methyl-2,4-pentanedione (**13**) produced the *exo*-methylene enamine **14** which was relatively stable under its conditions of formation. The enamine **14** underwent thermal rearrangement at 175° to 5-(2-phenylethyl)-1,3,4-trimethylpyrazole (**16**), evidently by a different type of process.

While the reaction of 3,3-disubstituted 2,4-pentanediones with hydrazine to give isopyrazoles is well known,[1,2] reaction of such substituted diketones with substituted hydrazines is imperfectly understood. Bis-2,4-dinitrophenylhydrazones[3–5] and bisphenylhydrazones[6] are usually formed, although 1:1 addition[7] and lack of reaction[8] have also been reported. Condensations with monoalkylhydrazines have apparently not been studied.

Reaction of 3,3-di(2-propynyl)-2,4-pentanedione (**1**) with methylhydrazine (*ca.* 1:1 mol ratio) in refluxing ethanol containing aqueous acetic acid gave a 72% yield of a crystalline base, $C_{12}H_{14}N_2$, corresponding to a loss of 1 mol of water from the hypothetical carbinolamine **2**.[9] The infrared (ir) spectrum of the product



(1) I. I. Grandberg, A. P. Krasnoshchek, A. N. Kost, and G. K. Faizova *J. Gen. Chem. USSR*, **33**, 2521 (1963).

(2) K. Auwers and F. Bergmann, *Ann.*, **472**, 287 (1929).

(3) M. F. Ansell, W. J. Hickinbottom, and A. A. Hyatt, *J. Chem. Soc.*, 1592 (1955).

(4) T. A. Favorskaya, A. V. Marshueva, and T.-Y. Hsü, *J. Gen. Chem. USSR*, **30**, 2499 (1960).

(5) J. J. Bloomfield, *J. Org. Chem.*, **26**, 4112 (1961).

(6) A. E. Favorskii and A. S. Onishchenko, *J. Gen. Chem. USSR*, **11**, 1111 (1941).

(7) C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Amer. Chem. Soc.*, **80**, 6533 (1958).

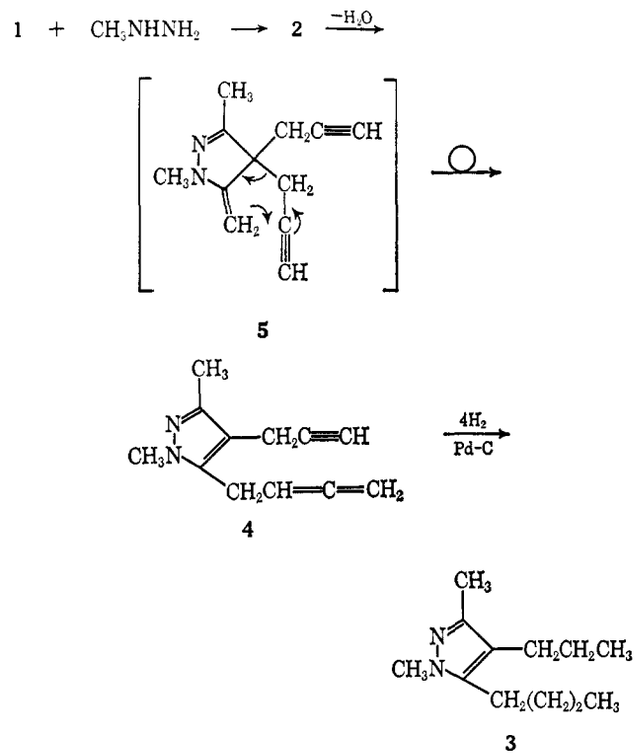
(8) G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, **127**, 797 (1925).

(9) P. Bouchet, J. Elguero, and R. Jacquier [*Tetrahedron*, **22**, 2461 (1966)] describe preparation of a related carbinolamine by reduction of the corresponding 5-pyrazolone.

indicated propargyl and cyclic C=CC=N functions and, most interestingly, the presence of an allenic group (5.1, 11.58 μ). The latter was shown by the nmr spectrum to be a butadienyl group $H_2C{=}C{=}CHCH_2{-}$ giving three multiplets at δ 3.29–3.45 (CH_2), 4.59–4.84 ($=CH_2$), and 4.94–5.39 ppm (=C—H) and the presence of one propargyl and two methyl groups was also evident. A maximum at about 225 mμ (ϵ 814) was seen in the uv, while the mass spectrum showed a parent peak at 186. The appearance of an unconjugated allene group together with evident aromatization to a pyrazole (ir, uv, nmr) indicates that a cyclic migration–rearrangement of one propargyl group has taken place.

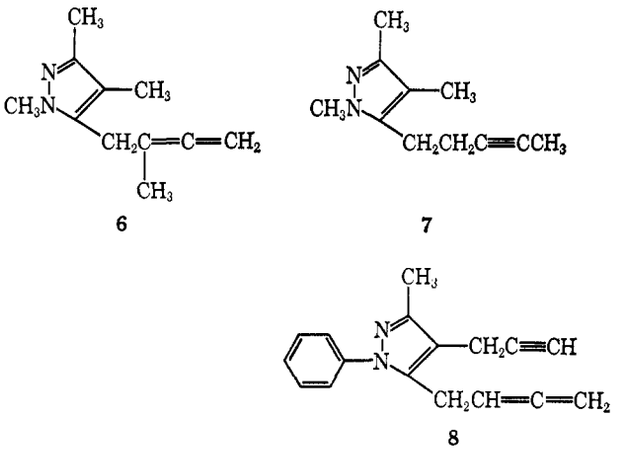
Catalytic reduction of $C_{12}H_{14}N_2$ required 4 mol of hydrogen and produced a base, identified by spectral and combustion analyses as 5-butyl-1,3-dimethyl-4-propylpyrazole (**3**). This information, along with the spectral data of $C_{12}H_{14}N_2$, indicates the structure of the product to be that of 5-(2,3-butadienyl)-1,3-dimethyl-4-(2-propynyl)pyrazole (**4**).[10]

The formation of a 2,3-butadienyl side chain in **4** suggests the occurrence of a new variant of the Claisen–Cope rearrangement involving the intermediate enamine **5** as follows.

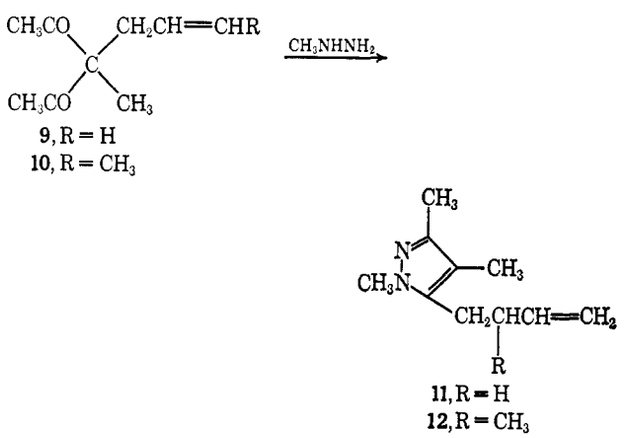


In similar fashion, methylhydrazine reacted with 3-(2-butynyl)-3-methyl-2,4-pentanedione giving only **6** (*ca.* 98% yield) with no evidence of the acetylenic isomer **7**. When the diketone **1** was treated with the less basic phenylhydrazine, the same rearrangement occurred, giving **8**.

Since Claisen rearrangements of olefinic functions are better known than those involving propargyl groups,



reaction of methylhydrazine with 3-allyl-3-methyl-2,4-pentanedione (**9**) and with 3-crotyl-3-methyl-2,4-pentanedione (**10**) was investigated. Smooth formation of pyrazoles **11** and **12** occurred with the exclusive appearance of the product (**12**) of crotyl inversion in-



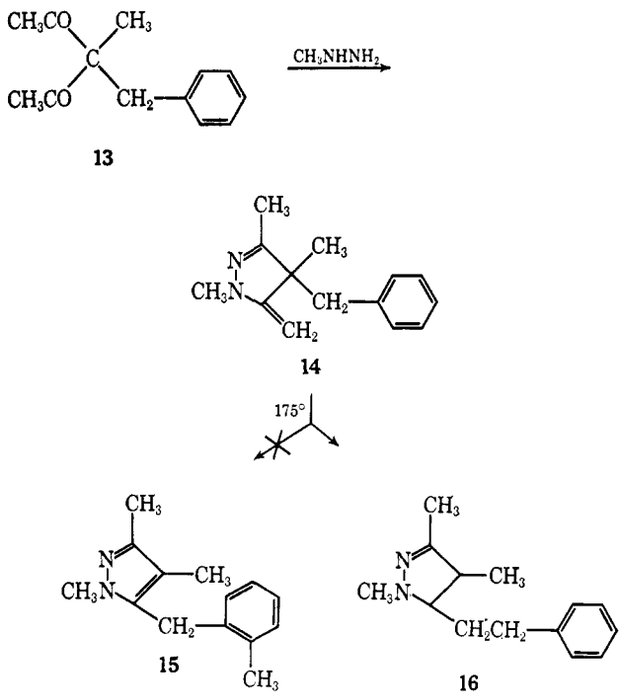
dicating the occurrence of a cyclic intramolecular rearrangement mechanism. Of additional interest was the reaction of methylhydrazine with 3-benzyl-3-methyl-2,4-pentanedione (**13**), since the expected enamine **14** should be potentially capable of (a) benzyl cleavage[11,12] by an ionic or radical mechanism and (b) Claisen rearrangement to the 5-*o*-tolyl product **15**. Action of methylhydrazine on **13** in refluxing ethanol, in fact, afforded **14** in 60% yield with no evident products of benzyl cleavage. When **14** was heated to 170–175°, however, an exothermic reaction occurred producing **16** in 85% yield. No trace of the hypothetical Claisen product **15** could be detected. It is thus apparent that migration of benzyl groups involves a process qualitatively distinct from the rearrangement of allylic or propargylic groups.

The present allylic and propargylic rearrangements are evidently facilitated by enaminic electron donation from a C-5 methylene group and can be visualized as involving a six-membered cyclic transition state whose energy is decreased by synchronous formation of a stable pyrazole ring. While it might seem, *a priori*,

(10) The spectroscopic data of **3** and **4** do not preclude alternative attachment of the C_3 and C_4 chains at pyrazole positions C-5 and C-4, respectively. In the absence of known reference derivatives for comparison our structural assignment is based upon a consideration of the structures of the possible pyrazole products and of their known intermediate precursors.

(11) Y. Makisumi, *Tetrahedron Lett.*, 6413 (1966). The possibility that thermal rearrangement of an allyloxypyrazole occurs by a dissociation–recombination process rather than by a concerted mechanism has also been considered by O'Brien and Gates.[12]

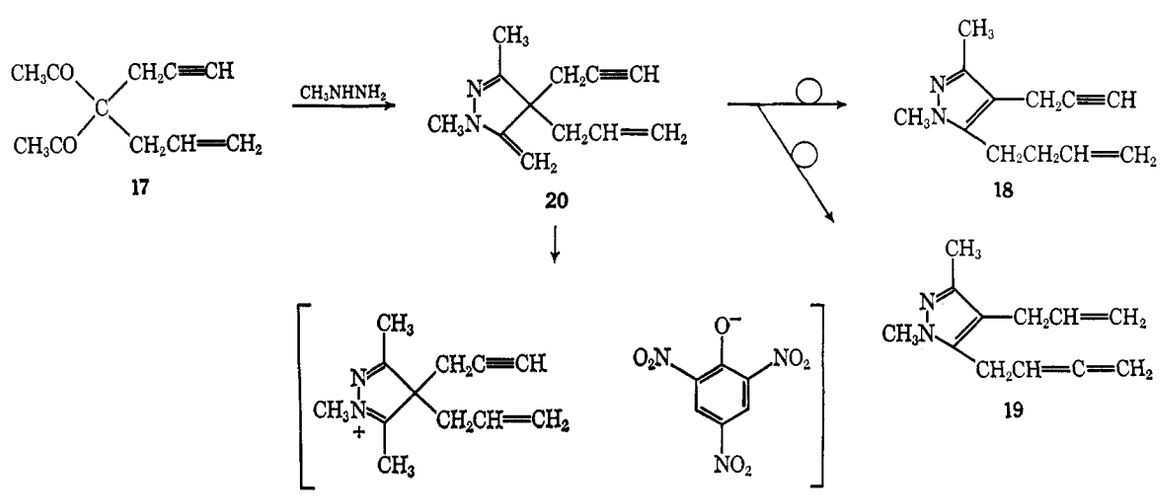
(12) D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.*, **31**, 1538 (1966).



13 14 15 16

difficult to accommodate such a transition state to linear propargyl and allenyl groups, similar propargylic rearrangements have been observed, although at temperatures higher than those presently employed.[13-15]

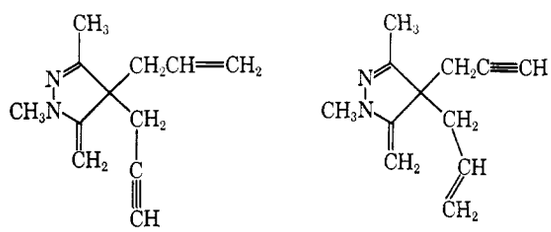
Since both propargyl and allyl groups rearrange readily under our present conditions, the reaction of methylhydrazine with 3-allyl-3-(2-propynyl)-2,4-pentanedione (**17**) was studied in order to obtain some idea



17 20 18 19 21

of the relative abilities of the two groups to rearrange. When the diketone **17** was treated with methylhydrazine at room temperature, vpc analysis of the reaction mixture at intervals showed concurrent formation of the products of allyl (**18**) and propargyl (**19**) rearrangement in the approximately constant ratio of 1.6:1. An ir spectrum of the reaction mixture after 23 hr showed strong bands corresponding to **18** (C≡C—H at 3.05 μ), to **19** (>C=C=C< at 5.15 μ), and to the enamine **20** (C=CH_2 at 6.1 μ), and the composition of the mixture, estimated from its nmr spectrum, was **18** (41%), **19** (34%), and **20** (25%). Upon refluxing the mixture for 1 hr in ethanol, a decrease in **20** with a corresponding increase in **19** was observed. Both **18** and **19** were thermally stable at the temperature (175°) of the gas chromatograph; hence the product ratio of 1.6:1 evidently represents a ratio of rate constants.[16] Final verification of the intermediate enamine (**20**) was obtained by repeating the reaction at 0° after which the pure picrate (**21**) of **20** was readily isolated. While structural assignments of **18** and **19** are made without recourse to independent syntheses, it would be difficult to postulate the formation of other products from **20**.

Although the ability of the propargyl group to compete so well with allyl in the rearrangement is surprising, consideration of the rotational modes of allyl and propargyl groups suggests an explanation. In orientation **20a** leading to propargyl rearrangement the rigid propargyl group can swing out of the bond-forming



20a 20b

position only by rotation about the propargylpyrazoline sp^3 bond at C-4, while rotation about the linear C—C≡C axis has no effect upon sp availability. Allyl rearrangement orientation (**20b**), however, requires correct rotational orientation about the two sp^3 bonds of the more flexible allyl group. Therefore, it may be argued that any steric disadvantages existing for propargylic Claisen–Cope rearrangement should be mitigated by an entropy factor favoring propargyl.

While Claisen-type rearrangements of allyl derivatives of pyrazoles[12] and of other nitrogen heterocycles[17,18] have been reported, formation of heteroaromatic systems *via* a carbon to carbon Claisen–Cope-type

(13) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 6784 (1965).
(14) R. Gardi, R. Vitalli, and P. P. Castelli, *Tetrahedron Lett.*, 3203 (1966).
(15) B. S. Thyagarajan, K. K. Balasubramanian, and R. Brima Rao, *ibid.*, 1393 (1963).

(16) Since vpc analysis of the final reaction product gave no indication of *ca.* 25% enamine (**20**), it is evident that part of the **18** and **19** measured result from decomposition of **20** in the chromatograph. Hence the 1.6:1 ratio represents a composite ratio for temperature ranging between 25 and 175°.
(17) J. K. Elwood and J. W. Gates, Jr., *J. Org. Chem.*, **32**, 2956 (1967).
(18) B. S. Thyagarajan, *Advan. Heterocycl. Chem.*, **3**, 143 (1967).

rearrangement appears to be novel as does the migration of allyl groups to an enaminic β carbon from a site other than nitrogen.[19] The present rearrangement of propargylic groups under extremely mild conditions is seemingly without precedent.[20]

Pyrazoles with allenic substitution have apparently not been described in the literature. The present reaction provides a synthetic route to such C-5 allenic derivatives and to other unsymmetrically substituted pyrazoles.

Experimental Section

Nuclear magnetic resonance spectra were determined with Varian A-60 and HA-100 instruments employing TMS as the internal reference. An Aerograph Model 202B dual-column gas chromatograph was used for vpc analysis. Ordinary molecular weight determinations were performed by a modification of the thermistor method of Neumayer.[21] All melting points are corrected.

Preparation of 3,3-Disubstituted 2,4-Pentanediones.—Stepwise alkylation of 2,4-pentanedione by the method of Johnson, *et al.*,[22] proved highly effective in preparing 3,3-di(2-propynyl)-2,4-pentanedione (**1**),[23] 3-allyl-3-methyl-2,4-pentanedione (**9**),[1] 3-benzyl-3-methyl-2,4-pentanedione (**13**),[1] and other starting 3,3-disubstituted 2,4-pentanediones.

3-(2-Butenyl)-3-methyl-2,4-pentanedione (**10**) had bp 58° (0.75 mm). *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.70; H, 9.65.

3-(2-Butynyl)-3-methyl-2,4-pentanedione had bp 76° (1.8 mm). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.44.

3-Allyl-3-(2-propynyl)-2,4-pentanedione (**17**) had bp 98° (5.8 mm). *Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.81; H, 7.99.

5-(2,3-Butadienyl)-1,3-dimethyl-4-(2-propynyl)pyrazole (**4**).—A solution of 3,3-di(2-propynyl)-2,4-pentanedione (2.64 g, 0.015 mol), methylhydrazine (0.78 g, 0.017 mol), glacial acetic acid (0.025 ml), and water (5 ml) in 75 ml of ethanol was refluxed for 3.5 hr, then evaporated under a stream of nitrogen. Crystallization of the residue from hexane at −80° gave 2.02 g (72.3%) of **4** as pale yellow crystals: mp 40–40.5°; ir (KBr) 3.05 (C≡C—H), 3.35, 3.41 (CH_3, CH_2), 4.73 (C≡C), 5.1 (C=C=C), 6.4 (C=C—C=N), 7.25 (C—CH_3), 11.5 μ (=CH_2 allene wagging); nmr ($CDCl_3$) δ 1.94 (t, 1, J = 2.8 Hz, C≡C—**H**), 2.20 (s, 3, CH_3—C=N), 3.62 (d, 2, J = 2.8 Hz, CH_2C≡C), 3.29–3.45 (m, 2, CH_2—C=C=C<), 3.70 (s, 3, CH_3—N<), 4.59–4.84 (m, 2, H_2C=C=C<), 4.94–5.39 (m, 1, —CH=C=C<); *m/e* 186 (parent), 147 (loss of $CH_2C{\equiv}CH$), 132 (loss of CH_3 from 147), 51 (C_4H_3 ion). *Anal.* Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04; mol wt, 186. Found: C, 77.12; H, 7.58; N, 14.85; mol wt, 182.

Compound **4** was sensitive to air at room temperature and sintered to a dark gum unless stored under nitrogen. Upon treatment with HCl in pentane, **4** gave a monohydrochloride, mp 112–114° (from ethyl acetate). *Anal.* Calcd for $C_{12}H_{15}N_2Cl$: C, 64.71; H, 6.79; N, 12.58. Found: C, 64.55; H, 7.04; N, 12.98.

The salt possessed an ir spectrum similar to that of **4** but with NH^+ bands at 3.83 and 3.95 μ. The nmr spectrum was essentially that of **4** with an additional proton (exchangeable) appearing at δ 14.6.

5-Butyl-1,3-dimethyl-4-propylpyrazole (**3**).—A solution of 2.0 g (0.0107 mol) of **4** in 50 ml of ethanol was hydrogenated at 25° (*ca.* 760 mm) in the presence of 5% Pd on carbon (0.1 g) causing uptake of about 4 mol of hydrogen. Distillation of the crude product gave 0.88 g of **3**: bp 155° (12 mm); *m/e* 194 (parent); ir (KBr) 6.35 μ (C=C—C=N); nmr ($CDCl_3$) δ 0.71–1.12 (t, 6, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$), 1.12–1.70 [m, 6, >(CH_2)CC(=C)—, >(CH_2CH_2)CC=C<], 2.15 (s, 3, CH_3—C=N), 2.26–2.72 [m, 4, >(CH_2)C=C(CH_2)<], 3.69 (s, 3, CH_3—N<). The picrate of **3**, recrystallized from methanol, melted at 91.5–93° and gave the following analysis. *Anal.* Calcd for $C_{18}H_{25}N_5O_7$: C, 51.06; H, 5.95; N, 16.54. Found: C, 51.00; H, 5.99; N, 16.58.

5-(2-Methyl-2,3-butadienyl)-1,3,4-trimethylpyrazole (**6**).—Methylhydrazine (2.4 g, 0.052 mol) and 3-(2-butynyl)-3-methyl-2,4-pentanedione (6.64 g, 0.04 mol) were allowed to react as described previously, employing a 7.5-hr reflux period. The residue product was dissolved in ethyl ether and dried ($MgSO_4$), and ether was removed to give a product which crystallized on standing. Recrystallization from pentane (cooling to −80°) gave 5.6 g of pure **6** (100% purity by vpc): mp 41.5–43°; nmr ($CDCl_3$) δ 1.61 (t, 3, J = 3 Hz, CH_3C=C=CH_2), 1.89 (s, 3, CH_3C=C<), 2.15 (s, 3, CH_3C=N—), 3.20 [t, 2, J = 3 Hz, —(CH_2)C=C=CH_2], 3.69 (s, 3, CH_3—N), 4.58 [sextet, 2, J = 3 Hz, H_2C=C=C(CH_3)CH_2—]; ir (KBr) 3.44, 3.5 (CH_3, CH_2), 5.10 (C=C=C), 6.35 (C=C—C=N), 7.24 (C—CH_3), 11.65 μ (C=C=CH_2 wagging). *Anal.* Calcd for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.89. Found: C, 74.79; H, 9.35; N, 15.96. A second crop of product, 1.4 g (96.3% purity by vpc), brought the total yield to 98.0%.

5-(2,3-Butadienyl)-3-methyl-1-phenyl-4-(2-propynyl)pyrazole (**8**).—Phenylhydrazine (11.9 g, 0.11 mol) and **1** (17.6 g, 0.10 mol) were allowed to react as above but employing butanol as the solvent with a reflux period of *ca.* 13 hr. An ether solution of the stripped residue was dried ($MgSO_4$) and chromatographed on alumina giving 20.45 g of crude **8** which crystallized from pentane on cooling to −80°. The solid (11.3 g, 45.3%) melted near room temperature to a red oil which was recrystallized (pentane) to give 5.3 g of pure **8**: ir (NaCl) 3.0 (C≡C—H), 3.25 3.4 (C—H), 4.7 (C≡C), 5.1 (C=C=C), 6.25, 6.65, 6.95 (C=C—C=N, phenyl C=C), 7.22 (C—CH_3), 11.78 (C=C=CH_2), 13.1, 14.4 μ (monosubstituted phenyl). *Anal.* Calcd for $C_{17}H_{16}N_2$: C, 82.22; H, 6.49; N, 11.28. Found: C, 82.30; H, 6.55; N, 11.41.

5-(3-Butenyl)-1,3,4-trimethylpyrazole (**11**).—3-Allyl-3-methyl-2,4-pentanedione (15.4 g, 0.1 mol) and methylhydrazine (5.06 g, 0.11 mol) were allowed to react under conditions identical with those described in the preparation of **4** giving, after evaporation of volatiles, an oil. An ether solution of the latter was dried ($MgSO_4$) and chromatographed on alumina giving 13.0 g (71.4%) of **11**: ir 6.05 (C=CH_2), 6.35 μ (C=C—C=N).

A 1.64-g (0.01 mol) portion of **11** yielded 3.34 g (85%) of a recrystallized (ethanol) picrate: mp 140.5–142.5°; nmr ($CDCl_3$) δ 2.04 (s, 3, CH_3C=C<), 2.39 (s, 3, CH_3C=N—), 2.15–2.57 [skewed quartet, 2, >(CH_2)C=C<], 2.68–3.00 (t, 2, >CH_2C=N<), 4.05 (s, 3, $CH_3\overset{+}{N}$<), 8.8 (s, 2, C_6H_2—), 15 (s, 1, exchangeable). *Anal.* Calcd for $C_{16}H_{19}N_5O_7$: C, 48.85; H, 4.87; N, 17.80. Found: C, 49.17; H, 4.69; N, 17.54.

5-(2-Methyl-3-butenyl)-1,3,4-trimethylpyrazole (**12**).—Methylhydrazine (1.5 g, 0.033 mol) and 3-crotyl-3-methyl-2,4-pentanedione (**10**, 5.0 g, 0.03 mol) were treated as before, employing butanol as solvent with a reflux period of 3.5 hr. The reaction residue was distilled under reduced pressure giving 3.25 g of **12** in the main fraction (95.7% by vpc), bp 64–65° (0.6 mm), and an additional 1.0 g in the forerun and in a final fraction as estimated by vpc. The total yield was 82.2%. The following spectral data were obtained: nmr ($CDCl_3$) δ 1.00 (d, 3, J = 6.5 Hz, CH_3C<), 1.88 (s, 3, CH_3C=C<), 2.14 (s, 3, CH_3C=N—), 2.49 (d, 2, $CH_2\overset{\|}{C}N$<), 2.4–2.6 (m, 1, tertiary H), 3.68 (s, 3, CH_3—N), 4.77–5.15 (m, 2, CH_2=C<), 5.5–6.08 (m, 1, —HC=C<); ir (KBr) 6.10 (C=CH_2), 6.35 (C=C—C=N), 10.05 (=CH *trans* wagging), 10.94 μ (=CH_2 wagging). The picrate, mp 103.5–104.5° (from ethanol), gave the following analysis. *Anal.* Calcd for $C_{17}H_{21}N_5O_7$: C, 50.12; H, 5.20; N, 17.19. Found: C, 50.17; H, 5.16; N, 17.26.

4-Benzyl-5-methylene-1,3,4-trimethyl-2-pyrazoline (**14**).—A mixture of methylhydrazine (5.06 g, 0.11 mol), 3-benzyl-3-methyl-2,4-pentanedione (20.4 g, 0.10 mol), acetic acid (1.0 ml), water (25 ml), and ethanol (200 ml) was refluxed for 4 hr, after which volatiles were removed giving 20.9 g of crude **14** as residue. A 5.0-g portion of the latter was dissolved in ether and chromatographed on an alumina column giving 3.1 g (60.5%) of pure **14**: nmr ($CDCl_3$) δ 1.17 (s, 3, CH_3C<), 1.86 (s, 3, CH_3C=N), 2.73 (s, 2, C_6H_5—CH_2), 2.89 (s, 3, CH_3—N), 3.67 (d, 2, J = 12 Hz, =CH_2), 7.11 (s, 5, C_6H_5); ir (KBr) 6.1

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(20) Propargyl → allenyl migration of **20** → **19** is actually observable, by ir analysis, after 17 hr at 0°.

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μ (N—C=CH_2). *Anal.* Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 78.12; H, 8.29.

5-(2-Phenylethyl)-1,3,4-trimethylpyrazole (16).—A 10.0-g sample of **14** was placed in a small distillation flask and heated to 172° under nitrogen. An exothermic reaction occurred with increase of the temperature to 210°, whereupon the heat was removed and the temperature fell to 165° in 17 min. An ether solution of the cooled residue was chromatographed (alumina) giving 8.5 g (85.0%) of pure **16**: bp 120–125° (0.15 mm); nmr ($CDCl_3$) δ 1.80 (s, 3, CH_3—C=C<), 2.14 (s, 3, CH_3-C=N—), 2.80 (s, 4, —CH_2—CH_2), 3.51 (s, 3, CH_3—N), 7.02–7.40 (m, 5, C_6H_5); ir (KBr) 13.32, 14.35 μ (monosubstituted phenyl). *Anal.* Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.40; H, 8.58; N, 13.20.

Reaction of Methylhydrazine with 3-Allyl-3-(2-propynyl)-2,4-pentanedione (17). A. In Refluxing Ethanol.—Methylhydrazine (5.06 g, 0.11 mol) and **17** (17.8 g, 0.1 mol) were allowed to react under the usual rearrangment conditions, but employing *ca.* a 15-hr reflux period. The solvent was evaporated, and a 16.5-g portion of the resulting oil (18.3 g) was chromatographed (ether elution) on alumina giving 14.6 g of **18** containing some of the allenic isomer (**19**) as indicated by absorption at 5.1 and 11.75 μ. Additional ir bands appeared at 3.0 (≡CH), 3.4 (C—H), 4.7 (C≡C), 6.4 (C=C—C=N), 7.2 (C—CH_3), 10.05 μ (=CH—), and 10.45 (=CH_2). A sample of product was converted into a picrate, mp 88–93° (51.2%), which, on recrystallization from ethanol, gave the picrate, mp 93.5–95.5°, of pure **18** showing no allenic absorption in the ir and nmr spectra: nmr ($CDCl_3$) δ 2.13 (t, 1, J = 2.8 Hz, H—C≡C), 2.47 (s, 3, CH_3—C=N), 2.44 (m, 2, CH_2—CH=CH), 2.90 (t, 2, J = 7.5 Hz, CH_2—CH_2CH=CH—), 3.41 (d, 2, J = 2.8 Hz, CH_2C≡C), 4.06 (s, 3, CH_3—N), 4.9–5.4 (m, 2, CH_2=C), 5.46–6.1 (m, 1, C=CH—), 8.90 (s, 2, C_6H_2), 14.08 (s, 1, exchangeable). *Anal.* Calcd for $C_{18}H_{19}N_5O_7$: C, 51.80; H, 4.59; N, 16.78. Found: C, 51.87; H, 4.48; N, 16.73.

Free **18** was isolated from its picrate by stirring 1.0 g of the latter with excess aqueous-ethereal HCl for 15 min followed by basification with NaOH and recovery by ether extraction. The yield of pure **18**, a yellow oil, was 410 mg (90.8%): ir (NaCl) 3.0 μ (≡C—H), 4.7 (C≡C), 6.07 (C=CH_2), 6.36 (C=C—C=N).

From a similar reaction of methylhydrazine with **17**, a reaction product was obtained, as above, consisting of **18** and **19**. A vpc analysis (5% Carbowax on 60–80 mesh Chromosorb W. AW, column temperature 175°) revealed peaks at 6.2 min (35.9% area) and 8.1 min (57.8% area). Enrichment of the mixture with pure **18** (from picrate, above) caused enlargement of the major (57.8%) peak. A sample of the minor (35.9%) component was collected by preparative vpc and shown to be the allenic isomer (**19**) by the following ir (KBr) data: 3.35, 3.42 (CH_3, CH_2), 5.11 (C=C=C), 6.4 (—C=C—C=N—), 7.25 (C—CH_3), 11.85 μ (allenic =CH_2).

The thermal stability of 5-(3-butenyl)-1,3-dimethyl-4-(2-propynyl)pyrazole (**18**) was tested by heating a sample at 172–175° for a 1-hr period followed by vpc and ir analyses. Although a pure sample of 4-allyl-5-(2,3-butadienyl)-1,3-dimethylpyrazole (**19**) was not available, a mixture containing *ca.* 66.5% **19** and 28.9% **18** was recovered from a mixture of the corresponding picrates and similarly subjected to the thermal treatment. Neither **18** nor the **19** + **18** mixture showed any change in ir or vpc following thermal treatment.

B. In Ethanol at Room Temperature.—The above-described reaction of methylhydrazine and **17** was performed at room temperature with subsequent vpc analysis (5% Carbowax 1540 on 60–80 mesh Chromosorb W. AW, column temperature 175°) of the mixture at 0-, 1-, 2-, 3-, 4-, 5-, 6-, and 23-hr intervals. The t = 0 sample showed substantial formation of **18** (7.1 min peak) and **19** (5.5 min peak) in an area ratio of about 1.62:1 which remained essentially constant as **18** and **19** increased over the 23-hr interval. At the end of the reaction, the mixture was rapidly evaporated at *ca.* 25° under reduced pressure. Infrared analysis showed, in addition to **18** and **19**, a C=O band (5.85 μ) and strong enamine absorption at 6.1 μ. Column chromatography (alumina) of an ether solution removed most of the carbonyl component with essentially no effect upon the other constituents as indicated by ir analysis. An nmr spectrum of the mixture showed the enamine **20** as a distinct singlet at δ 3.05 (CH_3—N<). Compound **19** showed a distinct multiplet at 4.59–4.76 (C=C=CH_2), and the corresponding integrals enabled the following estimate of composition: **20** (25%); **19** (34%); **18** (41%, by difference).

A sample of the chromatographed reaction product was refluxed in ethanol for 1 hr, and, after removing solvent, the ir spectrum was again determined. The enaminic 6.1-μ band was still present although notably weaker than before reflux, while a corresponding intensification of the allene (5.1, 11.8 μ) bands had occurred.

C. In Ethanol at 0°.—The above reaction was repeated at 0°, storing the mixture under nitrogen for a 17-hr period. Evaporation of volatiles left 19.0 g of material showing a strong enamine band (6.1 μ). Alumina chromatography afforded a 16.3-g fraction of oil showing very weak allenic absorption (5.1 μ) and and intense band at 6.1 μ. Treatment of 5.64 g (0.03 mol) of the material with picric acid (7.60 g, 0.03 mol) in ethanol at 0° gave 9.95 g of a crude picrate, mp 105–119°. A 1.75-g portion of the latter was recrystallized twice from ethanol giving 0.5 g (22.7%) of the pure picrate **21**: mp 135–136°; nmr (CD_3COCD_3); δ 2.44 (s, 3, CH_3—C=N—N), 2.73 (t, 1, J = 2.7 Hz, C≡C—H), 2.91 (s, 3, CH_3—C=$\overset{+}{N}$<), 2.98–3.12 (m, 2, CH_2—CH=CH), 3.20 (m, 2, CH_2C≡C), 4.16 (s, 3, CH_3—$\overset{+}{N}$), 5.02–5.6 (m, 3, CH=CH_2), 8.60 (s, 2, C_6H_2); ir (KBr) 3.03 (≡C—H), 6.1 (C=N, C=C), 6.44, 7.35 (NO_2), 7.05 (N—CH_3), 7.18 μ (C—CH_3). *Anal.* Calcd for $C_{18}H_{19}N_5O_7$: C, 51.80; H, 4.59; N, 16.78. Found: C, 51.93; H, 4.29; N, 16.70.

Registry No.—**3**, 17512-04-8; **3** picrate, 17512-05-9; **4**, 17512-06-0; **4** HCl, 17512-07-1; **6**, 17512-08-2; **8**, 17528-40-4; **10**, 17512-09-3; **11** picrate, 17512-10-6; **12** picrate, 17512-11-7; **14**, 17512-12-8; **16**, 17512-13-9; **17**, 17512-14-0; **18**, 17528-41-5; **18** picrate, 17528-42-6; **19**, 17512-15-1; **21** picrate, 17528-43-7; 3-(2-butynyl)-3-methyl-2,4-pentanedione, 17512-16-2; **12**, 17512-17-3.

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