140°. Recrystallization from benzene gave white crystals of **3**: mp 140–141° (lit.[11] mp 140–141.5°); picrate mp 158–160° (lit.[11] mp 157.5–159°); ir ($CHCl_3$) 2780, 1660, 1640, 1610, 1570, 1480, 1420, 1380, 1350, 1255, 1230, 1164, 986, 885, 775, 735 cm^{-1} (in complete accord with literature[12] ir); nmr ($CDCl_3$) δ 13.4 (broad s, 1, NH), 7.25 (d, 2, J = 7 Hz), 6.1 ppm (t, 1, J = 7 Hz) (in complete accord with literature[13] nmr).

Anal. Calcd for C_6H_7NO: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.24; H, 6.61; N, 12.88.

Vapor-Phase Pyrolysis of 1,3-Pentadienyl Isocyanate (1).—A 30 × 2.5 cm Pyrex column packed with glass helices and swept with a nitrogen stream was employed. The inlet was a septum cap allowing material to be syringe injected. The semisolid product obtained by the procedure for **1** above was taken up in $CHCl_3$ (20 ml). The oven was heated to 400° in a tube furnace and the material was injected in 1-ml portions with nitrogen sweeping the pyrolysate into a trap at −78°. Considerable carbonization was noticed in the pyrolysis zone. Ir analysis of the pyrolysate showed an intense band at 2300 cm^{-1} (**1**) but only a faint absorption at 1660 cm^{-1} (**3**). Peaks at 1770 (**6**) and 2150 cm^{-1} (**5**) had totally disappeared. Tlc analysis of the pyrolysate showed a faint spot of R_f corresponding to authentic **3** and an intense spot corresponding to **1** (silica gel, 10% *i*-PrOH in $CHCl_3$).

Pyrolysis of 3.—A solution of 50 mg of **3** in 1 ml of $CHCl_3$ was pyrolyzed in an identical fashion. No carbonization in the tube was observed, and the pyrolysate exhibited an unchanged ir spectrum.

Attempted Acid-Catalyzed Isomerization of 1.—A solution of *ca.* 250 mg of **1** in 5 ml of $CHCl_3$ exhibited an unchanged ir spectrum after being stored for 16 hr with 0.15 ml of trifluoroacetic acid. An additional 0.1 ml of CF_3CO_2H was added and the mixture was heated at reflux for 36 hr. The ir of the brown mixture showed no absorption at 2300 or 1660 cm^{-1}. The tlc showed no spot of R_f corresponding to **3**.

Tetrazolinone 6.—A refluxing solution of 4.9 g (0.037 mol) of **8** in 30 ml of heptane was treated over an 0.5-hr period with 5.8 g (0.05 mol) of trimethylsilyl azide. After 16 hr, 600 ml of N_2 had been evolved and a white powder had separated from the solution. Cooling and filtration gave 2.5 g (55%) of **6**: mp 161–162° (colorless crystals from benzene); ir ($CHCl_3$) 3030 (m), 1770 (s), 1730 (s), 1610 (s), 1600 (s), 1580 (s), 1500 (m), 1400 (m), 1380 (m), 1320 (s), 1250 (m), 1200 (s), 1140 (m), 1090 (m), 980 (m), 960 (s), 910 (m), 840 (m), and 640 cm^{-1} (s); nmr ($CDCl_3$) δ 7.6 (m, 1, HC=CC=O), 6.0–6.9 (m, 7, olefinic), 1.8 ppm (d of d, 6, J = 5 Hz, CH_3CH=C); uv max (heptane) 285 nm (log ϵ 4.4); uv max (heptane, OH^-) 265 nm (log ϵ 4.5); mass spectrum *m/e* (rel intensity) 247 (4), 246 (27), 152 (7), 137 (6), 109 (22), 95 (100), 81 (20), 80 (19), 67 (34), 54 (22), 41 (42), 39 (35).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 58.53; H, 5.73; N, 22.75. Found: C, 58.01; H, 5.42; N, 22.97.

Thermolysis of 6.—A solution of 50 mg of **6** in 3 ml of *o*-dichlorobenzene was heated at 180° for 16 hr. The solution turned brown and deposited a black polymeric material. Ir analysis showed the absence of absorption at 1770, 1730, and 1660 cm^{-1}, implying that **6** had been consumed but that **3** had not been formed.

Acknowledgments.—This investigation was sponsored under Grant No. CA-13120-01 from the National Cancer Institute. We thank Mr. John Simolike for obtaining the mass spectra.

Registry No.—**1**, 40711-07-7; **3**, 1003-56-1; **4**, 110-44-1; **6**, 40711-50-0; **8**, 2614-88-2.

(11) G. F. van Rooyen, C. Brink, and P. de Villiers, *Tydskr. Natuurwetensk.*, **4**, 182 (1964); *Chem. Abstr.*, **63**, 13202*d* (1965).

(12) E. Spinner and J. C. B. White, *J. Chem. Soc. B*, 991 (1966).

(13) C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocycl. Chem.*, **2**, 420 (1965).

Diaziridines. II. The Addition of Diaziridines to Electrophilic Acetylenes[1]

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Addition of 3,3-dialkyl-, 1,3-dialkyl-, and 1,3,3-trialkyldiaziridines to dibenzoylacetylene, diethyl acetylenedicarboxylate, and ethyl propiolate gives, generally, adducts in which the diaziridine ring is no longer intact. For example, addition of 1,3-dialkyl- and 1,3,3-trialkyldiaziridines to dibenzoylacetylene forms 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones (**2**). Evidence is presented that it is the alkylated nitrogen of 1-methyl-3,3-pentamethylenediaziridine which adds to the triple bond of dibenzoylacetylene. Stereochemical studies show that diaziridines add to ethyl propiolate to give trans adducts. Hydrolysis of 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones is shown to be a useful method for the preparation of 1-alkyl-3-phenyl-5-benzoylpyrazoles.

Only a few studies have been reported on the addition of N-unsubstituted or N-monosubstituted diaziridines to alkenes. Miller has found that 3-ethyl-3-methyldiaziridine adds to acrylonitrile and to butenone to form 1-(β-cyanoethyl)-3-ethyl-3-methyldiaziridine and 1-(β-acetylethyl)-3-ethyl-3-methyldiaziridine, respectively.[2] 1,3,3-Trialkyldiaziridines have been shown to react similarly with esters of ethenesulfonic acid.[3] The reaction of 3,3-pentamethylenediaziridine with diphenylcyclopropenone has also been described.[4] Based on the products of reaction it was presumed that the diaziridine added to the carbonyl group rather than the olefinic linkage

No investigations have yet been reported on the addition of diaziridines to electrophilic acetylenes. We have observed that, in contrast to aziridines which have been shown to add to a number of acetylenes to give *N*-vinylaziridines,[5] diaziridines usually react with activated acetylenes to give products in which the diaziridine ring is no longer intact.

Results

Diaziridines **1a–f** react with dibenzoylacetylene in benzene at ambient temperatures to give the 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones **2a–f** (Table I) (Scheme I).

The nmr spectra of **2a–f** were consistent with the proposed structures. Thus, a singlet (1 H) corresponding to the vinyl proton appeared in the region of δ 5.6–6.4 for all of these compounds. Furthermore, the

(1) For the previous paper in this series, see H. W. Heine, P. G. Williard, and T. R. Hoye, *J. Org. Chem.*, **37**, 2980 (1972).

(2) J. Miller, British Patent 1,081,292 (Aug 30, 1967); *Chem. Abstr.*, **68**, 114071h (1968).

(3) H. Dorn and K. Walter, *Justus Liebigs Ann. Chem.*, **720**, 98 (1968).

(4) J. W. Lown, *J. Chem. Soc. C*, 1338 (1969).

(5) O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, p 138.

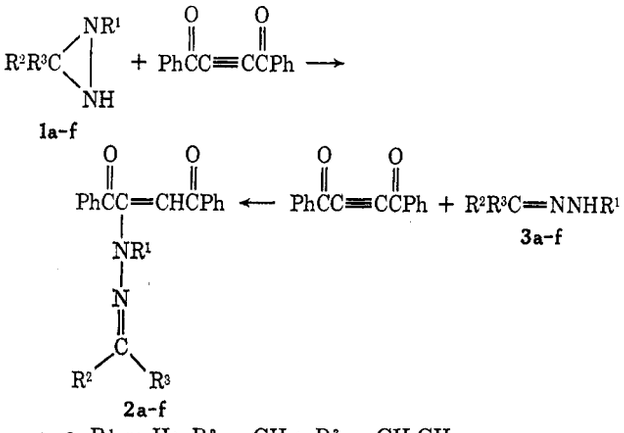
TABLE I

2-(ALKYLIDENEHYDRAZINO)-1,4-DIPHENYL-2-BUTENE-1,4-DIONES FROM THE REACTION OF DIBENZOYLACETYLENE WITH DIAZIRIDINES[a]

	$R^2R^3C{=}NN(R^1)C(COC_6H_5){=}CHCOC_6H_5$				
Compd	R^1	R^2	R^3	Crude yield, %	Mp, °C
2a	H	CH_3	CH_3CH_2	87	97–100
2b	CH_3	CH_3	CH_3	17	143–145
2c	$(CH_3)_2CH$	CH_3	CH_3	47	180–181
2d	CH_3	$CH_2CH_2CH_2CH_2CH_2$		98	114–119
2e	$CH_3CH_2CH_2CH_2$	H	CH_3CH_2	68	142–143
2f	$CH_3CH_2CH_2CH_2$	H	$CH_3CH_2CH_2$	68	86–88

[a] Satisfactory analytical data for C, H, and N were reported for all new compounds listed in the table: Ed.

SCHEME I



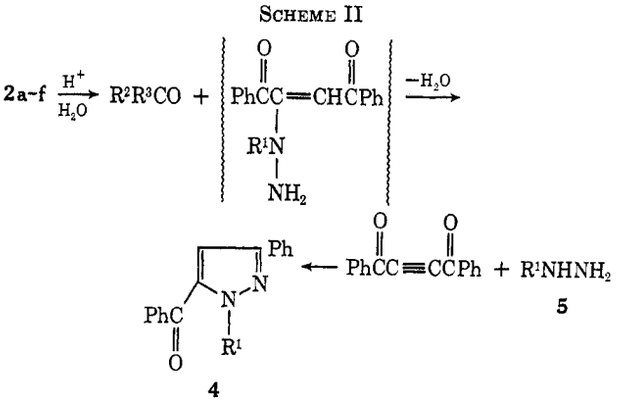
a, $R^1 = H$; $R^2 = CH_3$; $R^3 = CH_3CH_2$
b, $R^1 = R^2 = R^3 = CH_3$
c, $R^1 = (CH_3)_2CH$; $R^2 = R^3 = CH_3$
d, $R^1 = CH_3$; $R^2R^3 = -(CH_2)_5-$
e, $R^1 = CH_3(CH_2)_3$; $R^2 = H$; $R^3 = CH_3CH_2$
f, $R^1 = CH_3(CH_2)_3$; $R^2 = H$; $R^3 = CH_3CH_2CH_2$

nmr spectra of **2e** and **2f** exhibited two triplets centered at approximately δ 3.8 (2 H) and 7.1 (1 H). The downfield triplets in both these cases were assigned to the N=CH protons and the upfield triplets were assigned to the methylene groups bonded to the saturated nitrogen atom.

The structures of **2a–f** were unequivocally established by an alternate synthesis involving the addition of the corresponding hydrazones **3a–f** to dibenzoylacetylene (Scheme I).

Further confirmation for the structures assigned to **2a–f** was obtained by the acid hydrolysis of these substances into 1-alkyl-3-phenyl-5-benzoylpyrazoles (**4**) (Scheme II). These pyrazoles were also prepared by

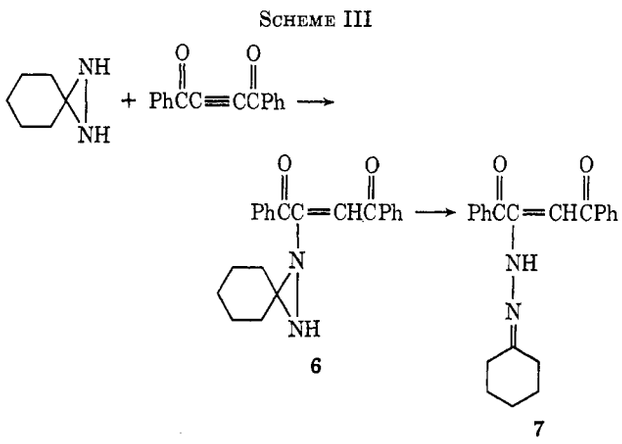
SCHEME II



adding appropriate alkylhydrazines (**5**) to dibenzoylacetylene. The hydrolysis of **2a–f** is a reaction of synthetic importance because the position of the N substituent relative to the other substituents on the pyrazole ring is unequivocal. Some of the methods employed in the past to form N-substituted pyrazoles (such as the alkylation or arylation of unsymmetrically substituted pyrazoles) yield two isomeric products often difficult to separate.[6] The preferred method of preparation of **4**, at least for the present, is the addition of *N*-alkyldiaziridines to dibenzoylacetylene followed by the hydrolysis of the resulting **2**. This method is more convenient than the addition of **5** to dibenzoylacetylene since many of the alkylhydrazines **5** are not readily available except by the hydrolysis of the corresponding diaziridines.

One diaziridine, namely, 3,3-pentamethylenediaziridine, added to dibenzoylacetylene in benzene to form **6**, a product in which the diaziridine ring is still intact (Scheme III). However, with but mild heating

SCHEME III



in 95% ethanol, **6** rapidly rearranged to **7**. Compound **6** also rearranged into **7** in a nmr tube containing chloroform and 1 drop of deuterium oxide.

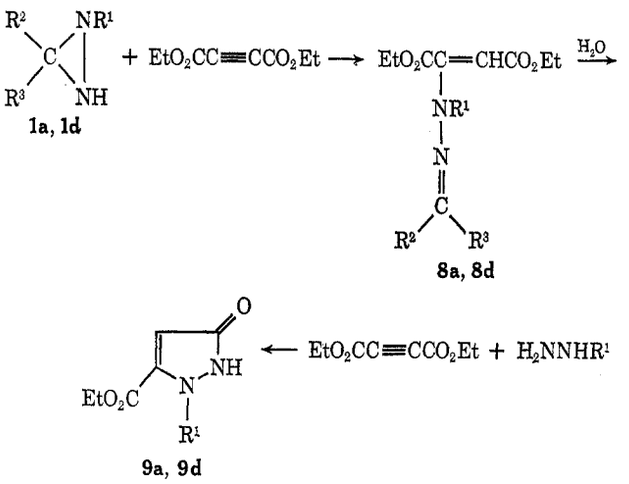
The structures of **6** and **7** were confirmed by nmr spectroscopy. In particular, the splitting pattern of the ring protons of **6** and of 1-methyl-3,3-pentamethylenediaziridine were quite similar. In both compounds the ring protons appear as a broad band with about the same chemical shift of δ 1.2–1.9. On the other hand, the aliphatic protons of **7** appear as two broad multiplets at δ 1.4–1.8 and 2.0–2.6 which is the same pattern observed for the cyclohexylidene moiety in **2d**, cyclohexanone methylhydrazone, and cyclohexanone oxime.

Diaziridines **1a** and **1d** were added to diethyl acetylenedicarboxylate to yield oily products presumed to be

(6) L. C. Bear, R. Fusco, and C. H. Jarboe, "Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings," R. H. Wiley, Ed., Interscience, New York, N. Y., 1967, pp 5–8.

8a and **8d**, respectively. The crude oils were characterized by hydrolyzing them to the known 3-carboethoxypyrazolin-5-one (**9a**) and 2-methyl-3-carboethoxy-3-pyrazolin-5-one (**9d**) (Scheme IV). Com-

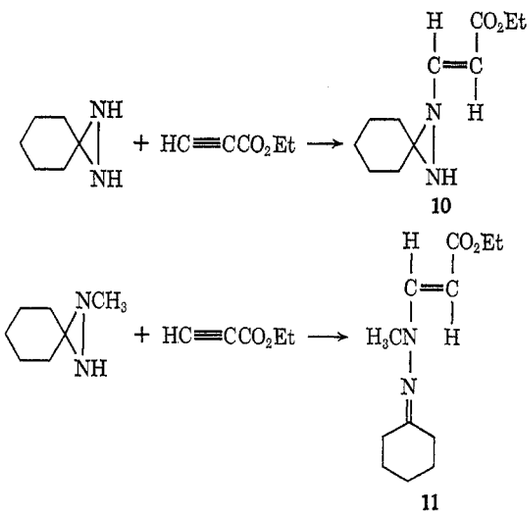
SCHEME IV



pounds **9a** and **9d** were also obtained by the addition of hydrazine and methylhydrazine to diethyl acetylenedicarboxylate.

3,3-Pentamethylenediaziridine and 1-methyl-3,3-pentamethylenediaziridine were also treated with ethyl propiolate in benzene to give **10** and **11**, respectively (Scheme V). Assignment of the trans configura-

SCHEME V



tion to **10** and **11** was made possible by using the results of earlier nmr investigations on adducts obtained from treating aziridine with ethyl propiolate[7] and from treating secondary amines with methyl propiolate.[8]

These studies established that the vinyl protons of ethyl 3-aziridinopropenoates and of methyl 3-dialkylaminopropenoates apear as an AB pattern with coupling constants of 8.0 Hz for the cis adducts and 13.0–13.4 Hz for the trans adducts.[7,8] Both compounds **10** and **11** in $CDCl_3$ gave nmr spectra with the expected AB pattern for the vinylic protons and with coupling constants of 13.0 Hz. However, the nmr spectrum of crude **10** revealed that a small quantity of the cis isomer (~10%) was also present since a second AB pattern was just discernible which had a coupling constant of 8.5 Hz. That compound **10** still had the diaziridine ring intact was deduced from its nmr spectrum (see reasoning employed for assigning the structure of **6**).

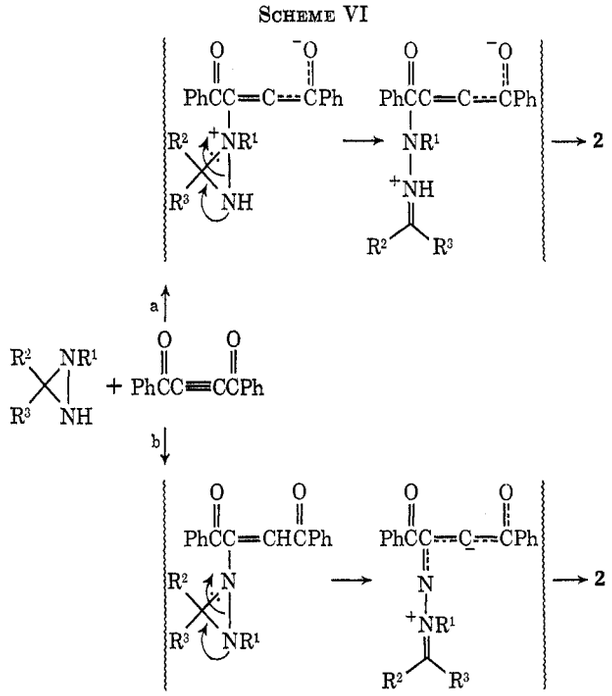
3,3-Pentamethylenediaziridine was also added to hexafluoro-2-butyne to give 1,1,1,4,4,4-hexafluoro-2-cyclohexylidenehydrazino-2-butene (**12**). Compound **12** was distillable and mass spectroscopy confirmed the molecular ion *m/e* to be 274.

Discussion

A Michael-type addition is undoubtedly involved in the reaction of diaziridines with electrophilic acetylenes. Indeed, in the case of the reaction of the 1,2-unsubstituted diaziridine, 3,3-pentamethylenediaziridine, with dibenzoylacetylene and ethyl propiolate, the addition products **6** and **10** are isolable. The demonstrated penchant of **6** to undergo facile conversion to **7** probably accounts for the Michael adduct not being isolated when the other 1,2-unsubstituted diaziridine used in this investigation, 3-ethyl-3-methyldiaziridine, was treated with dibenzoylacetylene.

The products **2b–f** formed when the 1,3-dialkyldiaziridines and 1,3,3-trialkyldiaziridines **1b–f** reacted with dibenzoylacetylene arise by the addition of the N-alkylated nitrogen (the most nucleophilic nitrogen) of the diaziridine to the alkyne linkage (pathway a, Scheme VI). Another mechanism in which the NH

SCHEME VI

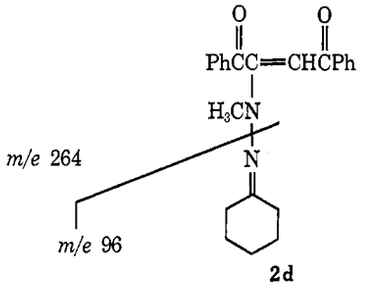


nitrogen of the diaziridine adds to the acetylenic carbon (such as pathway b) was discounted on the basis of the mass spectrum of the product obtained when 1-methyl-2-^{15}N-3,3-pentamethylenediaziridine was added to dibenzoylacetylene.

(7) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965).

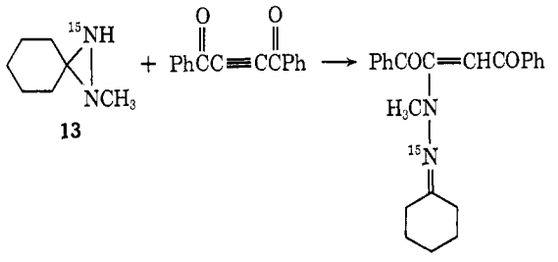
(8) (a) R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Ber.*, **99**, 2526 (1966); (b) A. N. Kurtz, W. E. Billups, R. P. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

The mass spectrum of the adduct **2d** showed cleavage fragments for the ions $(C_6H_{10}N)^+$, *m/e* 96, and $(C_{17}H_{14}NO_2)^+$, *m/e* 264. It is obvious that, if diaziridine **13** (Scheme VII) is added to dibenzoylacetylene, one



2d

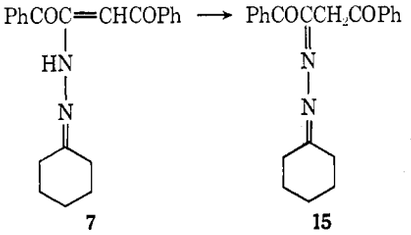
SCHEME VII



13 **14**

of the two cleavage peaks must increase by one mass unit according to which nitrogen of the diaziridine is bonded to the acetylene. Increase in the natural abundance of *m/e* 97 would be evidence for pathway a while increase in the natural abundance of *m/e* 265 would be evidence for pathway b of Scheme VI. Addition of **13** gave only **14** (see Experimental Section) proving unequivocally that the NCH_3 moiety of the diaziridine added to the triple bond directly.

It was observed that the nmr spectrum of **7** taken in $CDCl_3$ slowly changed over several hours. In particular, the vinyl absorption at δ 5.82 and the NH absorption at 13.3 diminished while a new peak at 4.33 appeared. This is most probably due to the isomerization of the enamine **7** into the tautomeric imine **15**.



7 **15**

The isomerization of imine–enamine tautomers obtained from the addition of phenylhydrazine to dimethyl acetylenedicarboxylate has recently been demonstrated.[9]

Experimental Section

Compounds 2a–f (Method A).—To a solution of 2–5 mmol of the known diaziridines (**1a–f**)[10] in 20 ml of dry benzene was added in portions an equivalent quantity of dibenzoylacetylene. The reaction mixture was stirred for 2 hr at room temperature and the solvent was evaporated to give usually a colored oil. In the case of **2a** the oil was dissolved in a minimum of hot 1:1 mixture of dry benzene–petroleum ether (bp 100–115°). After 2 days in the refrigerator, **2a** precipitated and was filtered. In the cases of **2b–f** the oils solidified upon standing in a hood for a day or so. Alternatively, the oils were dissolved in a minimum quantity of warm absolute ethanol. The ethanolic solution was cooled and the crystals of **2b–f** were filtered.

Compound 2a (Method B).—A suspension of 218 mg (2.53 mmol) of butanone hydrazone[11] in dry benzene was added dropwise to a solution of 593 mg (2.53 mmol) of dibenzoylacetylene in 15 ml of dry benzene. The reaction mixture was stirred for 1 hr and the solvent evaporated. A yield of 112 mg (14%) of **2a** was obtained.

Compound 2b (Method B).—A mixture of 169 mg (3.66 mmol) of methylhydrazine and 20 ml of dry acetone was stirred for 1 hr. To this mixture was added portionwise and with stirring 856 mg (3.65 mmol) of dibenzoylacetylene. The solvent was evaporated and a few drops of absolute ethanol was added to the residual oil whereupon **2b** crystallized quantitatively and was filtered.

Compound 2c (Method B).—A mixture of 102 mg (0.5 mmol) of acetone isopropylhydrazone oxalate,[12] 118 mg (0.5 mmol) of dibenzoylacetylene, and 10 ml of dry benzene was refluxed for 4.5 hr. The mixture was filtered and the solvent evaporated to give a red oil which was slurried in a small quantity of absolute ethanol. Crude **2c**, 80 mg (46%), crystallized after a few minutes and was filtered.

Compound 2d (Method B).—To a solution of 937 mg (4.0 mmol) of dibenzoylacetylene in 10 ml of dry benzene was added dropwise 504 mg (4.0 mmol) of cyclohexanone methylhydrazone.[13] The mixture was stirred for 2 hr and the solvent was evaporated. The residual dark oil crystallized upon the addition of a small quantity of ether. The crude **2d** (1070 mg, 74%) was filtered.

Compounds 2e–f (Method B).—A few milliliters of a concentrated sodium hydroxide solution was slowly added to a stirred suspension of 359 mg (2.0 mmol) of *n*-butylhydrazine oxalate in 10 ml of cold ether. The mixture was filtered and the filtrate was saved. The solid residue was washed with two 10-ml portions of ether and all of the ether filtrates were pooled. Five milliliters of propanal was added to the ether filtrates containing the *n*-Bu$NHNH_2$ and the solution was stirred for 1 hr before 314 mg (1.34 mmol) of dibenzoylacetylene was added portionwise. After 0.5 hr the solvent was evaporated to give 237 mg (49%) of crystalline **2e** based on the quantity of dibenzoylacetylene employed. Substitution of 5 ml of butanal gave a 22% yield of **2f**.

Pyrazoles 4 (Method A).—In general **2a–f** were dissolved in 10 ml of 95% ethanol containing 4 drops of concentrated hydrochloric acid. The reaction mixtures were refluxed for 0.5 hr and the solvent was evaporated to give the pyrazoles. Thus, 551 mg (1.72 mmol) of **2a** gave 360 mg (84%) of 3-phenyl-5-benzoylpyrazole,[14] mp 170.5–171°; **2b** (472 mg, 1.47 mmol) gave 200 mg (52%) of 1-methyl-3-phenyl-5-benzoylpyrazole, mp 52–57°; **2c** (680 mg, 1.95 mmol) gave 436 mg (77%) of 1-isopropyl-3-phenyl-5-benzoylpyrazole, mp 124–127°; **2d** (172 mg, 0.48 mmol) gave 76 mg (60%) of 1-methyl-3-phenyl-5-benzoylpyrazole, mp 52–57°; both **2e** (549 mg) and **2f** (487 mg) gave 1-*n*-butyl-3-phenyl-5-benzoylpyrazole as an oil (no yields taken).

3-Phenyl-5-benzoylpyrazole (Method B).—To a solution of 400 mg (1.71 mmol) of dibenzoylacetylene in 10 ml of absolute ethanol was added 55 mg of hydrazine hydrate. The reaction mixture darkened immediately and was stirred for 2 hr. The solvent was evaporated to give a quantitative yield of the pyrazole. Recrystallization from ethanol gave 3-phenyl-5-benzoylpyrazole melting at 170.5–171°.

1-Methyl-3-phenyl-5-benzoylpyrazole (Method B).—Methylhydrazine (46 mg, 1.0 mmol) was added dropwise to a solution of 234 mg (1.0 mmol) of dibenzoylacetylene dissolved in 10 ml of dry benzene. The reaction mixture was stirred for 1.5 hr and the solvent evaporated to give 100 mg (38%) of product. The pyrazole was recrystallized from absolute ethanol to give crystals melting at 52–57°.

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.98; H, 5.58; N, 10.44.

(9) N. D. Heindel and P. Kennewell, *J. Org. Chem.*, **35**, 80 (1970).

(10) We recommend the use of freshly prepared hydroxylamine-*O*-sulfonic acid rather than the commercially available product for the preparation of diaziridines.

(11) A. Kinnman, *C. R. Acad. Sci.*, **217**, 148 (1943).

(12) H. L. Lochte, W. A. Noyes, and J. R. Bailey, *J. Amer. Chem. Soc.*, **44**, 2556 (1922).

(13) R. H. Wiley and G. Irick, *J. Org. Chem.*, **24**, 1928 (1959).

(14) D. G. Farnum and P. Yates, *J. Amer. Chem. Soc.*, **84**, 1399 (1962).

1-Isopropyl-3-phenyl-5-benzoylpyrazole (Method B).—To a mixture of 116 mg (0.71 mmol) of isopropylhydrazine oxalate in benzene was added 165 mg (0.71 mmol) of dibenzoylacetylene. The mixture was heated until dissolution occurred. An equivalent quantity of solid potassium hydroxide was added to the reaction mixture, whereupon 122 mg (60%) of the pyrazole precipitated. Four recrystallizations from absolute ethanol gave 1-isopropyl-3-phenyl-5-benzoylpyrazole, mp 125–127°.

Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.58; H, 6.24; N, 9.64. Found: C, 78.53; H, 6.26; N, 9.78.

1-*n*-Butyl-3-phenyl-5-benzoylpyrazole (Method B).—A solution of 1.97 mmol of *n*-butylhydrazine in ether was prepared from *n*-butylhydrazine oxalate as described previously. To this solution was added an equivalent quantity of dibenzoylacetylene. The reaction mixture darkened immediately and it was stirred for 1 hr. Evaporation of the solvent gave a dark oil which could not be vacuum distilled. The ir and nmr spectra of the oil was identical with the spectra obtained from the hydrolysis of **2e** and **2f**.

Compound 6.—To a solution of 1.49 g (13.3 mmol) of 3,3-pentamethylenediaziridine in 20 ml of dry benzene was added 3.09 g (13.2 mmol) of dibenzoylacetylene. The reaction mixture was stirred for 1 hr and the solvent evaporated. The residual dark oil was dissolved in a small volume of warm, dry 1:1 benzene–petroleum ether (bp 100–115°). The solution after standing at 0° overnight gave 2.68 g (59%) of **6**. After four recrystallizations from the mixed solvent **6** was obtained which melted at 99–101°.

Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.43; H, 6.58; N, 8.18.

Compound 7.—Warming 222 mg of **6** for 2–3 min in 95% ethanol gave 209 mg of **7**, mp 123–125°. A sample of **6** in $CDCl_3$ containing 1 drop of water also rearranged into **7**. Four recrystallizations from absolute ethanol gave **7**, mp 124–125°.

Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.39; H, 6.41; N, 8.21.

3-Carboethoxypyrazolin-5-one (9a).—A mixture of 443 mg (5.14 mmol) of 3-ethyl-3-methyldiaziridine and 875 mg (5.14 mmol) of diethyl acetylenedicarboxylate in 10 ml of dry benzene was refluxed for 0.5 hr. The solvent was evaporated and the residual oil was dissolved in 10 ml of 95% ethanol containing 3 drops of concentrated hydrochloric acid. The mixture was refluxed for 1 hr and the solvent evaporated to give 687 mg (86%) of **9a**. Two recrystallizations from 95% ethanol gave **9a**, mp 184–187° (lit.[15] mp 184–185°).

2-Methyl-3-carbethoxy-3-pyrazolin-5-one (9d).—A mixture of 395 mg (3.14 mmol) of 1-methyl-3,3-pentamethylenediaziridine and 534 mg (3.14 mmol) of diethyl acetylenedicarboxylate in 10 ml of dry benzene was stirred for 0.5 hr. The solvent was evaporated and to the residual oil was added 10 ml of 95% ethanol containing 3 drops of concentrated hydrochloric acid. The mixture was refluxed for 0.5 hr and the solvent was evaporated to give 56 mg (10%) of **9d**. Four recrystallizations from absolute ethanol gave **9d**, mp 151–154°.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.40; H, 5.92; N, 16.47. Found: C, 49.47; H, 5.52; N, 16.40.

***trans*-Ethyl 3-(3,3-Pentamethylenediaziridino)propenoate (10).**—A mixture of 560 mg (5 mmol) of 3,3-pentamethylenediaziridine and 490 mg (5 mmol) of ethyl propiolate in 10 ml of benzene was stirred at room temperature for 48 hr. The solvent was evaporated and the residual oil was placed in a refrigerator. After several days 835 mg (79%) of **10** precipitated (attempts to recrystallize **10** were unsuccessful): molecular ion *m/e* 210; nmr ($CDCl_3$) δ 7.38 (d, 1, J = 13.0 Hz, NCH=), 5.68 (d, 1, J = 13.0 Hz, $CHCO_2$), 4.17 (q, 2, CH_2), 2.2–2.8 (m, 1, NH), 1.62 [s, 10, $(CH_2)_5$], 1.29 (t, 3 H, CH_3).

***trans*-Ethyl 3-(Cyclohexylidenemethylhydrazino)propenoate (11).**—A mixture of 630 mg (5 mmol) of 1-methyl-3,3-pentamethylenediaziridine and 490 mg (5 mmol) of ethyl propiolate in 10 ml of benzene was stirred for 12 hr. Evaporation of the solvent left 1.081 g (97%) of **11** as an undistillable oil: molecular ion *m/e* 224; nmr ($CDCl_3$) δ 7.38 (d, 1, J = 13.0 Hz, NCH), 4.50 (d, 1, J = 13.0 Hz, $CHCO_2$), 4.13 (q, 2, CH_2), 3.10 (s, 3, NCH_3), 2.17–2.60 [m, 4, $CH_2C(=N)CH_2$], 1.68 [s, 6, $CH_2(CH_2)_3CH_2$], 1.25 (t, 3, CH_2CH_3).

(15) S. Ruhemann, *J. Chem. Soc.*, **69**, 1395 (1896).

Compound **11** can also be prepared by mixing equimolar quantities of cyclohexanone methylhydrazone and ethyl propiolate in benzene and working up the reaction mixture as described above.

1,1,1,4,4,4-Hexafluoro-2-cyclohexylidenehydrazino-2-butene (12).—A stream of hexafluoro-2-butyne was slowly passed through a solution of 2.24 g (20 mmol) of 3,3-pentamethylenediaziridine in 9 ml of dry methylene chloride at −70°. After a slight excess of the acetylene was added the reaction mixture was stirred for 2.5 hr. The solvent was evaporated and the residual oil was distilled to give 3.36 g (62%) of **12**, bp 37–38° (0.15 mm), molecular ion *m/e* 274.

Anal. Calcd for $C_{10}H_{12}F_6N_2$: C, 43.80; H, 4.41. Found: C, 43.87; H, 4.58.

Preparation of 13.—A mixture of 0.5 g of hydroxylamine-^{15}N hydrochloride (95 at. % ^{15}N)[16] and 0.5 g of unlabeled hydroxylamine hydrochloride was ground with mortar and pestle and then transferred to a 10-ml beaker. Three milliliters of fuming sulfuric acid (30% SO_3) was added dropwise over a ten minute interval. The reaction mixture was cooled and 5 ml of cold, dry ether was added with stirring. The ^{15}N-enriched hydroxylamine-*O*-sulfonic acid was filtered immediately and washed with cold ether until it took on a fluffy appearance. The dry labeled hydroxylamine-*O*-sulfonic acid was then converted to 1-methyl-3,3-pentamethylenediaziridine according to a published procedure.[17] Specifically 1.4 g of the hydroxylamine-*O*-sulfonic acid enriched with ^{15}N was added to 14 ml of a cooled solution (0°) of 40% aqueous methylamine containing 1.47 g of cyclohexanone, over a time interval of 0.5 hr. The mixture was allowed to stand an additional hour at 0–10° and then extracted four times with 10-ml portions of ether. The extracts were dried over K_2CO_3 and the mixture was filtered. The ether was evaporated and the residue distilled to give 1.15 g of **13** boiling at 34–37° (0.75 mm). Compound **13** was then added to dibenzoylacetylene to yield **14**.

The labeled **14** showed a pair of molecular ion peaks, at *m/e* 360 and 361, in approximately equal abundance. Loss of one benzoyl group yielded fragment ions at *m/e* 255 and 256 for the ^{14}N and ^{15}N species. Cleavage between the two nitrogen atoms occurred most readily with charge retention on the *N*-methyldibenzoylethylene moiety yielding an intense ion (base peak) at *m/e* 264. This ion was not shifted in the mass spectrum of the ^{15}N-labeled product, indicating that the ^{15}N atom was located on the "cyclohexylimide" moiety. Cleavage between the nitrogens with charge retention on this fragment also occurred although the ion produced at *m/e* 96 was not so intense as the ion at *m/e* 264. Approximately equally intense ions at *m/e* 96 and 97 in the ^{15}N-labeled product confirmed the location of the label.

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Registry No.—**1a**, 4901-75-1; **1b**, 40711-15-7; **1c**, 17119-93-6; **1d**, 26177-34-4; **1e**, 40711-18-0; **1f**, 40711-19-1; **2a**, 40711-20-4; **2b**, 40711-21-5; **2c**, 40711-22-6; **2d**, 40711-23-7; **2e**, 40711-24-8; **2f**, 40711-25-9; **3a**, 29443-39-8; **3b**, 5771-02-8; **3c**, 7423-01-0; **3d**, 1567-83-5; **3e**, 20607-75-4; **3f**, 38126-74-8; **6**, 40711-31-7; **7**, 40711-32-8; **9a**, 40711-33-9; **9d**, 40711-34-0; **10**, 40711-35-1; **11**, 40711-36-2; **12**, 40711-37-3; **13**, 40711-38-4; **14**, 40711-39-5; dibenzoylacetylene, 1087-09-8; methylhydrazine, 60-34-4; acetone isopropylhydrazone oxalate, 40711-40-8; *n*-butylhydrazine oxalate, 40711-41-9; 3-phenyl-5-benzoylpyrazole, 21111-32-0; 1-methyl-3-phenyl-5-benzoylpyrazole, 40711-43-1; 1-isopropyl-3-phenyl-5-benzoylpyrazole, 40711-44-2; 1-*n*-butyl-3-phenyl-5-benzoylpyrazole, 40711-45-3; hydrazine, 302-01-2; isopropylhydrazine oxalate, 3468-25-5; *n*-butylhydrazine, 3530-11-8; 3,3-pentamethylenediaziridine, 185-79-5; diethyl acetylenedicarboxylate, 762-21-0; ethyl propiolate, 623-47-2; hexafluoro-2-butyne, 692-50-2; hydroxylamine-^{15}N hydrochloride, 40711-48-6.

(16) Isotopic Products, Merck Sharp and Dohme of Canada Ltd, Montreal, Canada.

(17) E. Schmitz, R. Ohme, and R. D. Schmidt, *Ber.*, **95**, 2714 (1962).