Studies on Heteroaromaticity. XLIV.[1] Reactivities of Benzoyl Cyanide *N*-Oxide and Some Derivatives Therefrom

Tadashi SASAKI, Toshiyuki YOSHIOKA, and Yasuyuki SUZUKI

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya

(Received July 13, 1970)

ω-Chloroisonitrosoacetophenone was treated with ethylenic and acetylenic dipolarophiles to afford 3-benzoylisoxazolinines and -isoxazoles, respectively. With *m*-nitrobenzaldoxime or *m*-nitrobenzonitrile, it yielded 3-benzoyl-5-(*m*-nitrophenyl)-1,2,4-oxadiazole. The phenylhydrazones of the 3-benzoylisoxazole and -oxodiazole thus produced were converted to the corresponding 1,2,3-triazoles thermally or by the treatment with a base. The photo-induced rearrangement of 3-benzoyl-5-phenylisoxazole afforded 2-benzoyl-5-phenyloxazole. Treatment of ω-chloroisonitrosoacetophenone with aziridine afforded a new type of aziridine oximes, which was converted to 2-benzoyloxazoline.

It is surprising that there have been no reports on the preparation and reactions of benzoyl cyanide *N*-oxide (I) in contrast to abundant reports on benzonitrile oxide, though ω-chloroisonitrosoacetophenone (II, phenylglyoxylyl chloride oxime) is a readily available compound[2] and is regarded as its precursor. Holleman[3] postulated the intermediary formation of I in the preparation of 1,5-dibenzoylfuroxan from acetophenone. Because of the presence of a carbonyl conjugated with the nitrile oxide group, I is thought to be stabilized by the resonance, but presumably reactive enough to undergo the 1,3-dipolar cycloaddition reactions. In this paper, the results in the 1,3-dipolar cycloaddition reactions are discussed in comparison with those in similar reactions of benzonitrile oxide. The thermal and basic rearrangement of the phenylhydrazones of 3-benzoylisoxazole and -oxadiazole thus produce and the photo-induced rearrangement of 3-benzoylisoxazole are discussed. The ring-enlargement of the aziridine adduct of I is also described.

Results and Discussion

1,3-Dipolar Cycloadditivity. In order to examine 1,3-dipolar cycloaddition reactivity, II was treated in ether with triethylamine in the presence of a dipolarophile (styrene, for example) according to the general procedure for preparing the nitrile oxides.[4] The oily product was characterized as 3-benzoyl-5-phenylisoxazoline (III) after conversion to its crystalline picrate on the basis of analytical and spectral evidences. A further evidence was provided by its conversion to crystalline 3-benzoylisoxazole (XVIII) with *N*-bromosuccinimide (NBS). A similar treatment of II with acrylonitrile afforded 3-benzoyl-5-cyanoisoxazoline (IV); IV showed no nitril absorption in the IR spectrum, which supports 5-cyano structure.[5] An attempt to convert it to isoxazole with NBS was unsuccessful. Acidic hydrolysis of IV with sulfuric acid gave benzoic acid, while 3-(5-nitro-2-furyl)-5-cyanoisoxazole (V) was convertible to the corresponding amide under similar conditions. Treatment of II with two equivalent amounts of 1-morpholino-2-cyanoethylene in ether at room temperature afforded 3-benzoyl-4-cyanoisoxazole (VI) similar to the 1,3-dipolar cycloaddition of aromatic hydroxamoyl chlorides to the enamine after spontaneous elimination of a morpholine molecule from the initial 1 : 1 adduct.[6] VI was hydrolyzed to amide under acidic conditions. Treatment of II with *o*-aminophenol and methyl anthranilate afforded linear adducts, *N*-phenylglyoxylyl-*o*-aminophenol oxime (VII) and methyl *N*-phenylglyoxylylanthranilate oxime (VIII), respectively, but with *o*-phenylenediamine, a cyclized product, 3-benzoyl-1,4-dihydro-1,2,4-benzotriazine (IX), instead of the expected benzoxazole[7] or quinazoline[8] and benzimidazole[7] in the similar reactions of aromatic hydroxamoyl chlorides. VIII was cyclized, however, to 3-hydroxy-4-oxo-2-benzoyl-3,4-dihydroquinazoline (X) on treatment with hydrochloric acid. With 1-cyano-2-diethylaminoacetylene,[10] II afforded 3-benzoyl-4-cyano-5-diethylaminoisoxazole (XI) as in the case of aromatic hydroxamoyl chlorides,[9] but with ammonium thiocyanate in methanol, II unexpectedly[10] yielded *N*-benzoylthiourethane (XII). Since the products III and IV could be obtained by the thermal 1,3-dipolar cycloaddition reactions of II in almost quantitative yields, the thermal reactions were performed using several dipolarophiles; the results are summarized in Table 1.

As seen from this table, ethylenic and acetylenic dipolarophiles reacted with II to give the corresponding isoxazolidines, III, IV, and XIII—XV, and isoxazoles, XVI—XX, respectively; the yield of the latter was lower because of the thermal instability.[11] It should be mentioned that the yield of the former was almost quantitative.

In order to compare the reactivity of II with that

1) Part XLIII of this series: T. Sasaki, K. Kanematsu, Y. Yukimoto, and S. Ochiai, *J. Org. Chem.*, in press.

2) "Org. Synth.," Col. Vol. **3**, 191 (1955).

3) A. F. Holleman, *Ber.*, **20B**, 3359 (1887); **21B**, 2835 (1888).

4) For instance, see R. Huisgen and W. Mack, *Tetrahedron Lett.*, **1961**, 583.

5) The quenching effect of nitrile absorption intensity is greater when the oxygen-containing group is attached to the same carbon atom as the nitrile, see L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., Ltd., New York (1969), p. 266.

6) T. Sasaki and T. Yoshioka, This Bulletin, **41**, 2212 (1968).

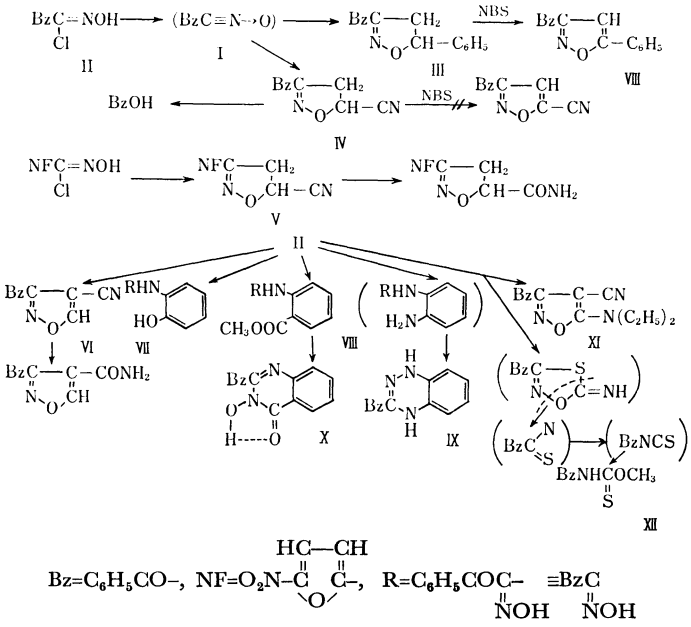
7) T. Sasaki and T. Yoshioka, *ibid.*, **42**, 3335 (1969).

8) T. Sasaki and T. Yoshioka, *ibid.*, **41**, 2206 (1968).

9) T. Sasaki and A. Kojima, *J. Chem. Soc., C*, **1970**, 476.

10) C. Musante, *Gazz. Chim. Ital.*, **68**, 331 (1938); T. Sasaki and T. Yoshioka, *Yukigosei Kagaku Kyokai-shi*, **27**, 877 (1969).

11) T. Sasaki and T. Yoshika, This Bulletin, **40**, 2604 (1967).



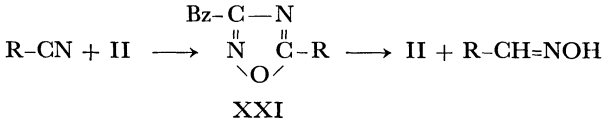
Bz=C_6H_5CO–, NF=O_2N–C_2H_2O–, R=$C_6H_5COC(=NOH)$–, ≡BzC(=NOH)–

TABLE 1. THERMAL 1,3-DIPOLAR CYCLOADDITION OF II

Dipolarophiles	Products	Mp °C	Reflux time hr	Yield %	Analysis Found (Calcd) C%	H%	N%	IR (KBr) CO cm^{-1}	NMR ($CDCl_3$) τ (coupling const) C-5	C-4	UV λ_{max}^{EtOH} mμ (ε)
Ethylenic											
Styrene	III	oil[b]	16	q[a]	61.94	3.85	16.08	1655	4.50	6.70	262 (35900)
					(61.25	3.97	16.24)		(10.5 Hz)		233 (21900)
Acrylonitrile	IV	73—74	20	q[a]	65.96	4.15	13.90	1640	4.54	6.19	
					(65.99	4.03	13.99)		(10.5 Hz)		
Acenaphthylene	XIII	132	30	q[a]	80.45	4.15	4.68	1640	3.38	4.27	
					(80.25	4.38	4.68)		(9 Hz)		
Indene	XIV	91—92	6	85	78.00	5.06	5.48	1640	3.79	5.49	
					(77.55	4.98	5.32)		(12 Hz)		
Acrylic acid	XV	106	22	80	59.85	4.05	6.46	1640	4.79	6.35	6.63 (CH_2)
					(60.27	4.14	6.39)		(9.8 Hz)		
Acetylenic											
Phenylacetylene	XVIII	91	8	q[a]	77.26	4.35	5.91	1650	—	2.92	
					(77.09	4.45	5.62)				
Diphenylacetylene	XVI	148	17	5	81.32	4.50	4.45	1660	—	—	
					(81.21	4.65	4.31)				
Propargyl alcohol	XVII	oil[c]	7	30	55.70	3.45	19.15	1650	—	—	
					(55.59	3.57	19.07)				
Propargyl bromide	XIX	60	15	80	49.40	3.07	5.25	1650	—	—	
					(49.65	3.03	5.27)				
1-Ethynyl cyclohexanol	XX	oil[c]	12	40	71.05	6.45	5.20	1650	—	3.30	
					(70.83	6.32	5.16)				

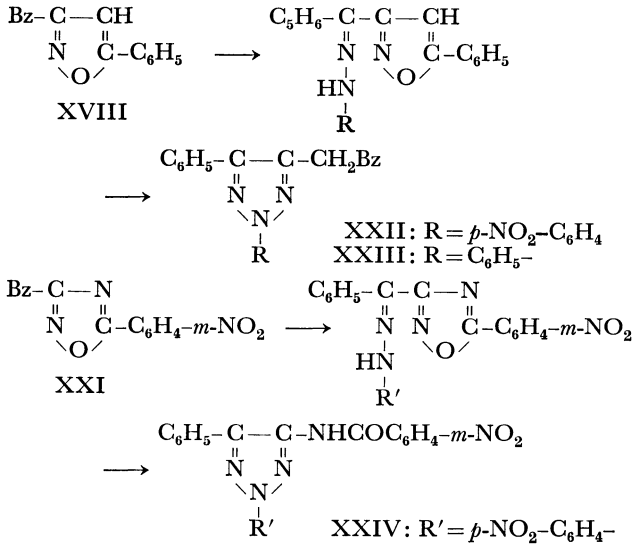
a) quantitative yields b) analyzed as picrate
c) Analyzed as dinitrophenylhydrazones, mp 156°C for XVII and mp 250°C for XX.

of hydroxamoyl chlorides, II was treated with benzamidine to afford 55% yield of 2,4,6-triphenyl-1,3,5-triazine, a trimer of benzamidine. This indicates no reactivity of II with benzamidine, with which hydroxamoyl chlorides are known to afford oxadiazoles.[7] With *m*-nitrobenzonitrile II afforded 15% yield of 3-benzoyl-5-(*m*-nitrophenyl)-1,2,4-oxadiazole (XXI), while the same compound was prepared from II and *m*-nitrobenzaldoxime in 50% yield. With *m*-nitrobenzaldehyde, II underwent no cycloaddition, while benzonitrile oxide affords the corresponding dioxazole.[4,8] Even taking into consideration these different reactivities from benzhydroxamoyl chloride, II might be concluded to be a good starting material for the preparation of 3-benzoylisoxazolines and -isoxazoles.



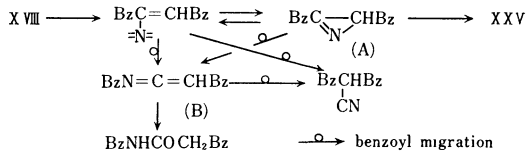
XXI

Rearrangement of 3-Benzoylisoxazole and 3-Benzoyloxadiazole. *a) Thermal and Basic Treatments*: Boulton *et al.*[12] have reported on the interesting thermal rearrangement reactions of one heterocycle to another as exemplified by those of 3-acetylisoxazole to 1,2,3-triazole *via* the phenylhydrazone and to 1,2,3-oxadiazole *via* the oxime. According to the modified procedure by Kano and Yamazaki,[13] *p*-nitrophenylhydrazone of XVIII was melted with copper powder to afford a quantitative yield of 2-(*p*-nitrophenyl)-4-phenyl-5-phenacyl-1,2,3-triazole (XXII), which was also obtained quantitatively by such a basic treatment as ammonia.[13] Similarly, 2,4-diphenyl-5-phenacyl-1,2,3-triazole (XXIII) was obtained from the phenylhydrazone of XVIII in 50% yield by thermal treatment. Thermal and basic treatments of the *p*-nitrophenylhydrazone of 3-benzoyl-1,2,4-oxadiazole (XXI) afforded 1,2,3-triazole (XXIV) in 60 and 90% yields, respectively. A similar rearrangement of *p*-nitrophenylhydrazone of VI failed, presumably because of the presence of a 4-substituent; thermal treatment afforded tarry polymer and the basic treatment resulted in recovery of the starting material. Attempts to obtain the oxime and the semicarbazone of XVIII were unsuccessful in contrast to the results given by Spiro and Ajello.[14]



b) Photochemical Treatment: One feature in the photo-induced rearrangement of five-membered heterocycles is that two vicinal heteroatoms can interchange their positions to 1,3-system when irradiated with ultraviolet light. This example involves the photo-induced rearrangement of 3,5-diphenylisoxazole to 2,5-diphenyloxazole[15] and that of benzisoxazole to benzoxazole,[16] but not that of 3-acylisoxazoles. Thus, XVIII (UV λ_{max}^{EtOH} mμ (ε): 262 (35900) and 233 (21900)) was irradiated at room temperature under nitrogen stream. Chromatography of the reaction mixture afforded 2-benzoyl-5-phenyloxazole (XXV), *N*-benzoylbenzoylacetamide, dibenzoylacetonitrile, benzoic acid and/or benzamide. The product distributions under different conditions are summarized in Table 2.

The thermal and basic rearrangement reactions of XVIII and XXI might be explained by the radical and ionic mechanisms proposed by Kano and Yamazaki,[13] and Ullman and Singh.[15] For photoinduced rearrangement of XVIII, a similar explanation for that from 3,5-diphenylisoxazole to 2,5-diphenyloxazole[15] can be applied by postulating the intermediacy of 2,3-dibenzoylaziridine (A) and/or *N*-benzoylbenzoylketenimine (B) after its benzoyl migration (⌒). The exclusive formation of benzoic acid in the reaction of XVIII in ethanol might be originated from hydrolytic photocleavage by contaminated water in the solvent.



Ring-enlargement. II was treated with two equivalent amounts of aziridine in ether at room temperature to afford oily *N*-phenylglyoxylylaziridine oxime (XXVI), which was converted to crystalline *O*-*p*-nitrobenzoate (XXVII). Since XXVI is regarded as a new type of aziridine oximes,[17] ring-enlargement was carried out. Thus, XXVI was refluxed in acetone with a catalytic amount of sodium iodide to give an oily amine, which was characterized as 2-benzoyloxazoline (XXVIII) after conversion to the crystalline picrate.

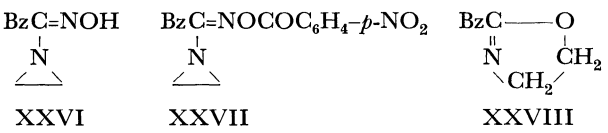
Table 2. Photochemistry of 3-benzoyl-5-phenylisoxazole (XVIII)
(Yields % based on the converted XVIII)

Solvent	Mercury lamp	Reaction time hr	Recovered XVIII	Product distributions				
				XXV	*N*-Benzoyl-benzoyl-acetamide	Dibenzoyl-acetonitrile	Benzoic acid	Benzamide
Benzene	60-W low pressure	42	10	23	28	3	2	—
Ether	60-W low pressure	18	29	30	—	8	6	—
Ethanol	60-W low pressure	24	0	—	—	—	56	28
Benzene	100-W high pressure[a]	30	70	10	—	—	17	7

a) Using a liquid filter No 5. A. Schonberg, "Preparative Organic Photochemistry," Springer-Verlag New York Inc. 1968, p. 491.

12) A. J. Boulton, A. R. Katritzky, and A. M. Hamid, *J. Chem. Soc., C*, **1967**, 2005.
13) H. Kano and E. Yamazaki, *Tetrahedron*, **20**, 159, 461 (1964).
14) V. Spiro and E. Ajello, *Ann. Chim.* (Rome), **58**, 128 (1968).
15) E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967). D. W. Kurz and H. Shechter, *Chem. Commun.*, **1966**, 689.
16) M. Ogata, H. Matsuno, and H. Kano, Abstract of the Symposium on the Chemistry of Heterocyclic Compounds, p. 157 (Osaka, Oct., 1968).
17) T. Sasaki and T. Yoshioka, This Bulletin, **42**, 556 (1969).

The yield of the conversion to XXVIII was improved up to 60% by treating with concd. hydrochloric acid in acetone at room temperature.[17]



XXVI XXVII XXVIII

Experimental

All melting points were determined on a Yanagimoto electric micromelting point apparatus and are uncorrected. The ultraviolet (UV) and infrared spectra (IR) were recorded on a Jeolco Model ORD/UV-5 and a Jasco Model IR-S spectrometer. The NMR spectra were determined on a Varian A-60 and a Jeolco MINIMAR, with tetramethylsilane as an internal standard and the peak positions are expressed by τ-values. Column chromatography was carried out on a silica-gel (Mallinckrodt, 100 mesh) using benzene as an eluent.

3-Benzoyl-5-phenylisoxazoline (III). *a) Nitrile Oxide Method*: To a stirred solution of 1.84 g (0.01 mol) of ω-chloroisonitrosoacetophenone (II)[2] and 1.04 g (0.01 mol) of styrene in 50 m*l* of ether was added a solution of 1.2 g (0.012 mol) of triethylamine in 10 m*l* of ether under cooling with ice-water. The reaction mixture was stirred at room temperature overnight. The resulting precipitates (triethylamine hydrochloride) were removed and the filtrate was concentrated. The residual oil was converted to the crystalline picrate, mp 219—220°C, and analyzed (Table I). The yield was 30%.

b) Thermal Treatment: A solution of the same amounts of the two components as above in 50 m*l* of toluene was refluxed for 16 hr. The solvent was removed and the residual oil was purified as above to give a quantitative yield of III (Table 1).

Its Conversion to 3-Benzoyl-5-phenylisoxazole (XVIII). A solution of 1.0 g of III and 0.75 g of *N*-bromosuccinimide (NBS) in 20 m*l* of carbon tetrachloride was refluxed in the presence of a trace of azobisisobutyronitrile (AIBN) for 3 hr. The reaction mixture turned from red to pale yellow. The mixture was filtered and the filtrate was concentrated. The residue was treated with a solution of 0.25 g of potassium hydroxide in 10 m*l* of methanol to afford 0.5 g (50%) of XVIII, mp 91°C, which was identical with a specimen pre pared from II and phenylacetylene (Table 1). Phenylhydrazone, mp 106—107°C.

Found: C, 77.93; H, 5.60; N, 12.54%. Calcd for $C_{22}H_{27}ON_3$: C, 77.85; H, 5.05; N, 12.38%.

p-Nitrophenylhydrazone, mp 191—192°C. UV λ_{max}^{EtOH} mμ (ε): 396 (31700), 278 (16300) and 250 (22100).

Found: C, 68.95; H, 4.35; N, 14.45%. Calcd for $C_{22}H_{16}O_3N_4$: C, 68.74; H, 4.20; N, 14.58%.

3-Benzoyl-5-cyanoisoxazoline (IV). IV was obtained from II and acrylonitrile by the nitrile oxide method in 30% yield, but by the thermal procedure quantitatively. (Table 1).

3-(5-Nitro-2-furyl)-5-cyanoisoxazoline (V) and Its Conversion to Amide. *Thermal treatment*: A solution of 0.95 g (5 mmol) of 5-nitro-2-furylhydroxamoyl chloride[11] and 1.0 g (20 mmol) of acrylonitrile in 40 m*l* of toluene was refluxed for 15 hr. The chromatography afforded 0.74 g (70%) of V, mp 109°C, by recrystallization from ethanol. IR (KBr): no nitrile absorption at around 2200—2400 cm^{-1}.

Found: C, 46.53; H, 2.57; N, 20.41%. Calcd for $C_8H_5O_4N_3$: C, 46.38; H, 2.43; N, 20.29%.

The same compound was obtained in 65% yield by the nitrile oxide method.

Conversion of V to the amide was carried out as follows: a solution of 0.3 g of V in 4 m*l* of concd. sulfuric acid was stirred at room temperature for 2 days. The reaction mixture was poured onto ice-water and the resulting yellow crystals were collected and recrystallized from ethanol - THF to afford the amide in 75% yield, mp 225°C, which was identical with a specimen[11] by IR comparison.

3-Benzoyl-4-cyanoisoxazole (VI). A solution of 1.84 g (0.01 mol) of II and 2.8 g (0.02 mol) of 1-morpholino-2-cyanoethylene[18] in 50 m*l* of ether was stirred at room temperature for one week. The resulting precipitates were filtered and the solvent was removed from the filtrate. The residual solid was recrystallized from *n*-hexane to give 60% yield of VI, mp 73—74°C. IR (KBr) cm^{-1}: 2250 (ν_{CN}), and 1660 (ν_{CO}). NMR ($CDCl_3$) τ: 0.09 (s, 1H, C_5-H).

Found: C, 67.04; H, 3.25; N, 14.07%. Calcd for $C_{11}H_6O_2N_2$: C, 66.66; H, 3.05; N, 14.14%.

Its Conversion to Amide. Similar as in the case of V, VI was treated with concd. sulfuric acid to afford the amide, mp 174—175°C, in 70% yield. IR (KBr) cm^{-1}: 3400, 3350 (ν_{NH}) and 1670 (ν_{CO}).

Found: C, 60.89; H, 3.80; N, 13.05%. Calcd for $C_{11}H_8O_3N_2$: C, 61.11; H, 3.73; N, 12.96%.

N-Phenylglyoxylyl-o-aminophenol Oxime (VII). Treatment of II with two equivalent amounts of *o*-aminophenol in ether at room temperature for 1 day afforded 70% yield of VII, mp 162—163°C, by recrystallization from a 10 : 1 mixture of benzene and ethanol. IR (KBr) cm^{-1}: 1660 (ν_{CO}).

Found: C, 66.17; H, 4.91; N, 10.57%. Calcd for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.72; N, 10.93%.

Methyl N-Phenylglyoxylylanthranilate Oxime (VIII). Similarly, a solution of 0.92 g (5 mmol) of II and 1.51 g (10 mmol) of methyl anthranilate in 70 m*l* of ether was left standing at room temperature for two months. Chromatography of the filtrate afforded 0.5 g (30%) of VIII, mp 162—164°C, by recrystallization from ethanol. IR (KBr) cm^{-1}: 3340 (ν_{NH}) and 1675 (ν_{CO}).

Found: C, 64.35; H, 4.75; N, 9.38%. Calcd for $C_{16}H_{14}O_4N_2$: C, 64.42; H, 4.73; N, 9.39%.

3-Benzoyl-1,4-dihydro-1,2,4-benzotriazine (IX). A similar treatment of II with *o*-phenylenediamine for 3 days afforded 75% yield of IX, mp 223—225°C, by recrystallization from a 3 : 1 mixture of benzene and ethanol. IR (KBr) cm^{-1}: 3200 (ν_{NH}) and 1640 (ν_{CO}).

Found: 71.03; H, 4.83; N, 17.57%. Calcd for $C_{14}H_{11}ON_3$: C, 70.87; H, 4.67; N, 17.71%.

Conversion of VIII to 3-Hydroxy-4-oxo-2-benzoyl-3,4-dihydroquinazoline (X). A solution of 0.2 g of VIII in 1 m*l* of concd. hydrochloric acid was warmed at 60—70°C in a sealed tube for 20 min. After cooling, the resulting crystals were collected and recrystallized from benzene - petroleum ether to afford 0.1 g (50%) of X, mp 76—78°C. IR (KBr) cm^{-1}: 3450, 2250 (broad, bound ν_{OH}[19]), 1670 and 1650 (ν_{CO}[8]).

Found: C, 67.75; H, 3.82; N, 10.60%. Calcd for $C_{15}H_{10}O_3N_2$: C, 67.66; H, 3.79; N, 10.52%.

3-Benzoyl-4-cyano-5-diethylaminoisoxazole (XI). Treatment of 1.84 g (0.01 mol) of II and 2.2 g (0.02 mol) of diethylaminocyanoacetylene[9] in 50 m*l* of ether at room temperature for one week afforded 40% yield of XI, mp 133—134°C, on chromatography. IR (KBr) cm^{-1}: 2240 (ν_{CN}) and 1650 (ν_{CO}).

18) T. Sasaki, T. Yoshioka, and K. Shoji, *J. Chem. Soc., C*, **1969**, 1086.

19) A. Dorner and K. Fisher, *Chem. Ber.*, **99**, 72 (1966).

Found: C, 66.90; H, 5.66; N, 15.62%. Calcd for $C_{15}H_{15}O_2N_3$: C, 66.90; H, 5.61; N, 15.61%.

N-Benzoylthiourethane (XII). A solution of 0.45 g (2.5 mmol) of II in 10 m*l* of methanol was added to a stirred solution of 0.35 g (5 mmol) of ammonium thiocyanate in 10 m*l* of methanol at room temperature. Chromatography afforded 0.3 g (70%) of XII, mp 98—99°C from benzene - petroleum ether, which was identical with a specimen prepared from benzoyl isothiocyanate and methanol.[20]

Reaction of II with Benzamidine. To a stirred mixture of a solution of 1.0 g of II in 30 m*l* of ether and a solution of 0.9 g of benzamidine hydrochloride in 20 m*l* of water was added a 5% aqueous potassium carbonate (1.6 g) under ice-cooling. Stirring was continued for 12 hr. Ether layer was separated, from which 0.6 g (55%) of 2,4,6-triphenyl-1,3,5-triazine, mp 240°C (lit,[21] 239°C) was isolated.

Found: C, 81.39; H, 5.03; N, 13.66%. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58%.

3-Benzoyl-5-(m-nitrophenyl)-1,2,4-oxadiazole (XXI). This was prepared by refluxing in toluene for 20 hr of II with *m*-nitrobenzaldoxime and *m*-nitrobenzonitrile in 50 and 15% yields, respectively. Mp 174—175°C. IR (KBr) cm^{-1}: 1675 (ν_{CO}).

Found: C, 61.00; H, 3.21; N, 13.98%. Calcd for $C_{15}H_9O_4N_3$: C, 61.02; H, 3.07; N, 14.23%.

The *p*-nitrophenylhydrazone: mp 294—295°C.

Found: C, 58.65; H, 3.35; N, 19.47%. Calcd for $C_{21}H_{14}O_5N_6$: C, 58.60; H, 3.28; N, 19.53%.

Thermal Rearrangement of The Hydrazones of XVIII. General procedure: the hydrazone was melted with 1/3 of its weight of copper powder in a vacuum at a temperature slightly higher than the melting point for 10 min. The residue was extracted with hot ethanol to give the corresponding triazole.

Thus, 2,4-diphenyl-5-phenacyl-1,2,3-triazole (XXIII) was obtained in 50% yield as an oil from the phenylhydrazone of XVI. IR (KBr) cm^{-1}: 1685 (ν_{CO}). NMR ($CDCl_3$) τ: 5.42 (s, 2H, $-CH_2-$). Its 2,4-dinitrophenylhydrazone, mp 210—211°C.

Found: C, 64.87; H, 4.22; N, 18.52%. Calcd for $C_{28}H_{21}O_4N_7$: C, 64.79; H, 4.08; N, 18.89%.

A similar treatment of the *p*-nitrophenylhydrazone of XVIII afforded a quantitative yield of 2-(*p*-nitrophenyl)-4-phenyl-5-phenacyl-1,2,3-triazole (XXII), mp 137—138°C. UV λ_{max}^{EtOH} mμ (ε): 332 (22300), 242 (14800), and 230 (14200). IR (KBr) cm^{-1}: 1680 (νC_{CO}). NMR ($CDCl_3$) τ: 5.38 (s, 2H, $-CH_2-$).

Found: C, 68.75; H, 4.33; N, 14.44%. Calcd for $C_{22}H_{16}O_3N_4$: C, 68.74; H, 4.20; N, 14.58%.

Basic Rearrangement. The *p*-nitrophenylhydrazone of XVIII was dissolved in a minimum amount of acetone containing one drop of concd. ammonium hydroxide. The solution was refluxed for 5 hr; during that time the solution was kept alkaline by occasional addition of concd. ammonium hydroxide to the solution. By this procedure a quantitative yield of XXII was obtained.

Thermal and Basic Treatment of The p-Nitrophenylhydrazone of XXI. Similar thermal and basic treatments afforded XXIV, mp 280—281°C. IR (KBr) cm^{-1}: 3180 (ν_{NH}) and 1670 (ν_{CO}).

Found: 58.95; H, 3.54; N, 19.25%. Calcd for $C_{21}H_{14}O_5N_6$: C, 58.60; H, 3.28; N, 19.53%.

Photochemistry of XVIII. General procedure: A 0.01 mol/*l* solution of XVIII in a given solvent was irradiated at room temperature under nitrogen stream for a given reaction time. The resulting precipitates were filtered and recrystallized from ethanol - benzene to afford XXV, mp 134—136°C. IR (KBr) cm^{-1}: 1650 (ν_{CO}).

Found: C, 76.77; H, 4.45; N, 5.17%. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62%.

The solvent was removed from the filtrate and the residue was chromatographed. The first fraction gave unreacted starting material. Then, dibenzoylacetonitrile, mp 160°C,[22] XXV and benzoic acid were successively isolated.

Dibenzoylacetonitrile. IR (KBr) cm^{-1}: 3400 (broad, ν_{OH})[23] and 2220 (ν_{CN}).

Found: C, 77.32; H, 4.47; N, 5.85%. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.45; N, 5.62%.

When XVIII was irradiated with a 60-W low pressure mercury lamp in benzene, the main product was *N*-benzoylbenzoylacetamide, mp 170°C.[24] IR (KBr) cm^{-1}: 3250 (ν_{NH}), 1705 and 1680 (ν_{CO}). NMR (DMSO-d_6) τ: −0.82 (NH) and 5.42 ($-CH_2-$).

Found: C, 71.55; H, 4.86; N, 5.53%. Calcd for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90; N, 5.24%.

The results are summarized in Table 2.

N-Phenylglyoxylylaziridine Oxime (XXVI) and Its O-p-Nitrobenzoate (XXVII). To a stirred solution of 0.92 g (0.005 mol) of II in 50 m*l* of ether was added dropwise a solution of 1 m*l* of aziridine in 50 m*l* of ether under ice-cooling. The mixture was stirred for 30 min at this temperature and then for 24 hr at room temperature. After removal of the precipitates, the filtrate was concentrated to give 80% yield of XXVI as an oil. IR (neat) cm^{-1}: 3325 (ν_{OH}). NMR ($CDCl_3$) τ: 7.64 (s, 1H, OH) and 7.74 (s, 4H, $-CH_2-CH_2-$).[25]

To a stirred solution of 0.5 g (0.0025 mol) of XXVI and 0.5 g (0.05 mol) of triethylamine in 40 m*l* of dry benzene was added a solution of 0.5 g (0.0025 mol) of *p*-nitrobenzoyl chloride in 20 m*l* of dry benzene under ice-cooling. The reaction mixture was left standing overnight. After the solution was saturated with dry hydrogen chloride gas, the precipitates were filtered and the filtrate was concentrated. The residue was chromatographed to afford 0.41 g (50%) of XXVII, mp 147—149°C, by recrystallization from benzene - petroleum ether. IR (KBr) cm^{-1}: 1750 and 1665 (ν_{CO}). NMR ($CDCl_3$) τ: 7.42 (s, 4H, $-CH_2-CH_2-$).[25]

Found: C, 59.93; H, 3.94; N, 12.40%. Calcd for $C_{17}H_{13}O_5N_3$: C, 60.17; H, 3.86; N, 12.39%.

2-Benzoyloxazoline (XXVIII). A solution of 0.7 g of XXVI in 30 m*l* of acetone was refluxed in the presence of 0.2 g of sodium iodide for 30 min. The filtered solution was concentrated and chromatographed to give an oil (XXVIII). IR (neat) cm^{-1}: 1640 (ν_{CO}) and 1610 ($\nu_{C=N}$). Its picrate, mp 179—180°C; the yield was 0.3 g (25%). NMR (DMSO-d_6) τ: 4.8—5.6 (m, 4H, $-CH_2-CH_2-$)[26] and 1.8—2.5 (m, 5H, phenyl protons).

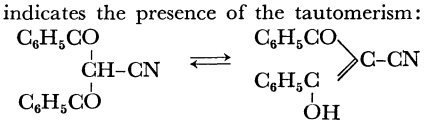
Found: C, 47.10; H, 3.24; N, 14.43%. Calcd for $C_{16}H_{14}O_9N_4$: C, 47.29; H, 3.47; N, 13.79%.

20) P. Miquel, *Ann. Chim.*, [v], **11**, 346 (1877).

21) B. W. Frizmmon, C. Hewlett, and R. A. Shaw, *J. Chem. Soc.*, **1965**, 47779.

22) Mp 156.5°C: E. v. Mayer, *J. prakt. Chem.*, [2], **42**, 267 (1890).

23) This indicates the presence of the tautomerism:



24) Mp 170°C: G. Sugowdz and G. Shaw, *J. Chem. Soc.*, **1954**, 665.

25) Equivalent two methylene protons of the aziridine ring are characteristics in these compounds. See H. Kessler, *Angew. Chem.*, **82**, 237 (1970).

26) Non-equivalent two methylene protons are a good proof of the aziridine ring rupture.