NMR (CCl_4) δ 1.37 (s, 6 H) and 2.65 (s, 5 H) [lit. NMR ($CDCl_3$) δ 1.35 (s, 6 H) and 2.65 (s, 5 H)].[16]

Reaction of 3 with DMAD. A mixture of 40 mg (0.354 mmol) of **3** and 47 mg (0.331 mmol) of DMAD in 4 ml of carbon tetrachloride was refluxed for 2 days and the solvent was removed in vacuo. Vacuum distillation gave 34 mg (46% yield) of dimethyl 2,6-dimethylpyridine-3,4-dicarboxylate (**17**): bp ca. 100° (10^{-3} mm); ir (CCl_4) 3000, 1745, 1600, 1580, 1445, 1380, 1325, 1270, 1220, 1160, 1085 cm^{-1}; NMR (CCl_4) δ 2.53 (s, 3 H), 2.57 (s, 3 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 7.33 (s, 1 H); mass spectrum (70 eV) *m/e* 223.0848 (calcd for $C_{11}H_{13}NO_4$; 223.0844); *m/e* (rel intensity) 223 (M^+, 2), 192 (10), 191(12), 159 (6), 133 (6), 128 (8), 101 (3), 100 (7), 85 (2), 68 (9), 59 (4), 58 (4), 44 (5), 43 (21), 42 (4), 41 (5), 40 (2), 39 (3), 32 (5), 31 (5), 29 (5), 28 (21), 27 (2), 18 (100), 17 (18), 15 (15).

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Registry No.—**1**, 23974-38-1; **3**, 54384-93-9; **4**, 52856-04-9; **6**, 54384-94-0; **8**, 49680-46-8; **10**, 54384-95-1; **11**, 54384-96-2; **16**, 23974-51-8; **17**, 54384-97-3; DMAD, 762-42-5.

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Photolysis of Azido-1,3,5-triazine. Photocycloaddition of Singlet Nitrene to Nitriles

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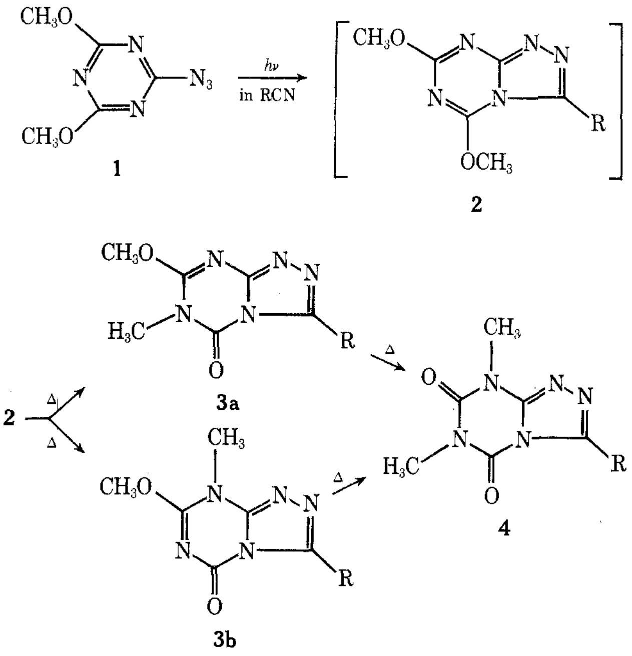
There has been considerable interest recently in the field of nitrene chemistry, and many nitrene reactions (addition to olefins, insertion into the C–H bond, ylide formation with Lewis bases, and other reactions) have been reported.[1] As for the reaction of nitrenes with nitriles, carbethoxynitrene[2,3] and acetylnitrene[4] add to the nitrile group to yield 1,3,4-oxadiazoles. However, little mechanistic work has been reported and photolysis of azido-1,3,5-triazine has not been studied. The reactivity of the triazinyl nitrene is unknown. Triazine derivatives give rise photochemically to interesting reactions: the photo-Smiles rearrangement,[5] the photo-Fries rearrangement,[6] and the phototriazinylation.[7] During the course of our studies on triazine photochemistry, we have carried out the photolysis of azidotriazine in nitriles, and observed the photocycloaddition of singlet triazinyl nitrene to the CN group.

The photolysis of 2-azido-2,4-dimethoxy-1,3,5-triazine (**1**) in degassed and aerated nitriles at 254 nm is shown in Scheme I. The photoproducts which could be isolated are listed in Table I.

Scheme I



$R_1 = CH_3$
$R_2 = C_2H_5$
$R_3 = C_6H_5$

The uv spectral change of **1**, for example, in acetonitrile (R_1CN) showed a great decrease in the λ_{max} (238 nm) of the starting material[8] and a slight increase in the 260–310-nm range during the photolysis. This change indicates that both **3aR**$_1$ (7-methoxy-3,6-dimethyl-*s*-triazolo[4,3-*a*]-1,3,5-triazin-5-one) and **3bR**$_1$ (7-methoxy-3,8-dimethyl-*s*-triazolo[4,3-*a*]-1,3,5-triazin-5-one) were not primary photoproducts, but were formed thermally from **2R**$_1$ (5,7-dimethoxy-3-methyl-*s*-triazolo[4,3-*a*]-1,3,5-triazine), because the absorption maxima of **2aR**$_1$ and **3bR**$_1$ are at 240 and at 255 nm, respectively. This result was confirmed by a change in the NMR spectra of the photolyzed solution[9] that occurred after standing at room temperature, and the appearance of only weak ir absorption at the characteristic 1735-cm^{-1} absorption of **3a** and **3b** immediately after irradiation.

Similarly, the photoadducts **3aR**$_2$ and **3bR**$_2$ (trace) were detected in the photolyzed solution of 1 in propionitrile (R_2CN). In the case of benzonitrile (R_3CN), the final product **4R**$_3$ (6,8-dimethyl-3-phenyl-*s*-triazolo[4,3-*a*]-1,3,5-triazine-5(6*H*),7(8*H*)-dione) was the only one isolated:[10] the analytical and spectral data agreed with those reported by Kobe et al.[11] The O → N shifts of methyl groups[12] in the photoproducts **2** took place easily even at room temperature. The lack of aromaticity in the compounds **2** and **3** may facilitate the O → N shifts of methyl groups, as has been suggested by Reynolds et al.[13] The O → N shift of

Table I
Properties of Starting Material and Photoadducts[d]

Substance	Chemical yield, %	Mp, °C	MS, *m/e*	NMR[c]
1		85–85.5[a]		4.05 (2,4-OCH_3)
3aR$_1$	7	153–154	195	2.47 (3-CH_3), 3.60 (6-CH_3) 4.22 (7-OCH_3)
3bR$_1$	15	155–156.5	195	2.80 (3-CH_3), 4.05 (7-OCH_3) 3.80 (8-CH_3)
3aR$_2$	17	153–154	209	1.37 (3 H), 2.88 (2 H), in 3-C_2H_5 3.60 (6-CH_3), 4.22 (7-OCH_3)
4R$_3$	2	213–214 (222–225)[b]	257	8.10 (2 H), 7.52 (3 H), in 3-C_6H_5 3.34 (6-CH_3), 3.58 (8-CH_3)

[a] See ref 17. [b] From Kobe et al., see ref 11. [c] In $CDCl_3$; for the NMR data of **2**, see ref 9. [d] Satisfactory analysis (±0.3% for C, H and N) were reported for **3aR$_1$** and **3bR$_1$**; for **3aR$_2$**, calcd N, 33.48; found, 32.87; for **4**, calcd C, 56.02, found, 55.58. Ed.

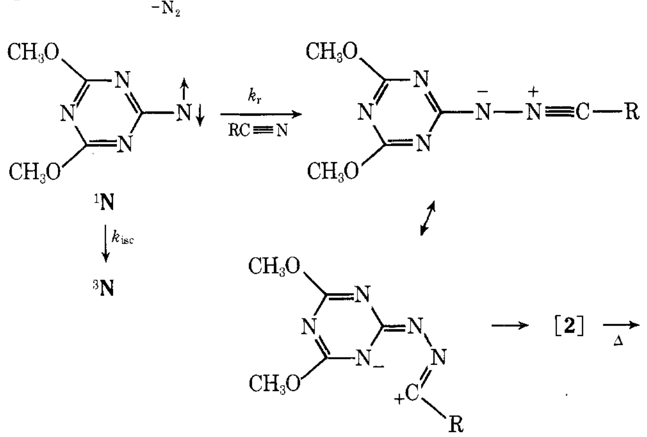
methyl group at the 5 position should occur more readily than that at the 7 position, since the anion generated by the heterolytic fission of OCH_3[12] at the 5 position is expected to be more stable than that at the 7 position.

The absorption spectrum (λ_{max} 313 nm, see Figure 1) of triplet triazinyl nitrene (^{3}**N**) was observed during the photolysis of **1** in a rigid EPA matrix at 77 K and at 254 nm: the ^{3}**N** should be formed via fast intersystem crossing in the singlet nitrene ^{1}**N**.[14] The lowest transition energy in ^{3}**N** (3.96 eV) was larger than that in triplet phenylnitrene (~3.35 eV) reported by Reiser et al.[14] The photosensitization of **1** in degassed R_1CN by triplet benzophenone has been carried out.[15] The sensitized photodecomposition of **1** took place to a large extent. However, the cycloaddition products shown in Table I could not be detected.[16] The quantum yields for the **2R$_1$** formation both in aerated and degassed R_1CN were close to unity (0.90 ± 0.10).

From these results, we conclude that the singlet triazinyl nitrene (^{1}**N**) attacks the cyano group in the nitriles. It is well known that singlet nitrenes are electrophilic,[1a] and this tendency in ^{1}**N** may be strengthened by the electron-withdrawing power of the triazinyl nucleus. The reaction rate $k_r[RCN]$ may be faster than the k_{isc} of the intersystem crossing $^1N \rightarrow {}^3N$.

Finally, the primary photochemical reactions can be accounted for by Scheme II, where ^{1}**1** denotes the excited singlet state of **1**.

Scheme II



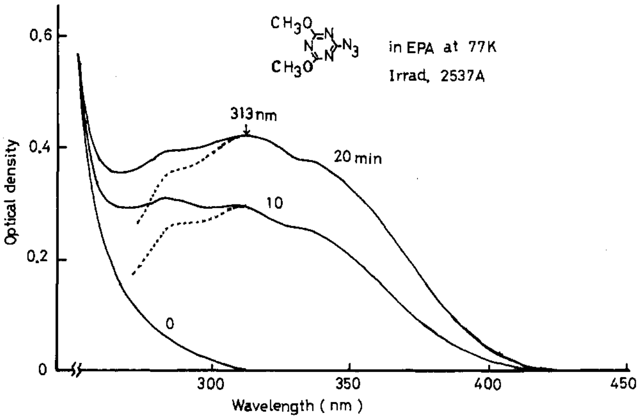


Figure 1. Spectral change of rigid EPA matrix of **1** at 77 K with lapse of time at 2537 Å. Numbers refer to time in minutes. Dotted lines denote the corrected absorption spectra of ^{3}**N**.

Experimental Section

Materials. The starting material 2-azido-4,6-dimethoxy-1,3,5-triazine (**1**) was prepared by treating 2-chloro-4,6-dimethoxy-1,3,5-triazine with NaN_3 and purified by repeated recrystallizations from benzene-ligroin.[17] The solvents were G. R-grade products of Tokyo Kasei Co. Ltd., and they were used without further purification. The solution of **1** was degassed by the freeze–pump–thaw method.

Light Sources and Actinometry. A 30-W low-pressure Hg lamp was used as the 254-nm radiation source. In the benzophenone photosensitization, a 100-W high-pressure Hg lamp was used with a glass cutoff filter (>310 nm). The actinometry was carried out using a ferric oxalate solution (0.006 *M*).[18] The amount of product **2R$_1$** was determined by means of NMR at the characteristic peak (δ 2.80) due to the methyl group on the 3 position in **2R$_1$**, calibrated against 2-chloro-4,6-bis(dimethylamino)-1,3,5-triazine (δ 3.10).

Registry No.—**1**, 30805-07-3; **2R$_1$**, 54410-40-1; **3aR$_1$**, 54410-41-2; **3aR$_2$**, 54410-42-3; **3bR$_1$**, 54410-43-4; **4R$_3$**, 28750-32-5; 2-chloro-4,6-dimethoxy-1,3,5-triazine, 3140-73-6; NaN_3, 26628-22-8.

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(8) ϵ 1.36 × 10^4 at 238 nm in acetonitrile.

(9) The NMR spectra of **2R$_1$** and **2R$_2$** in $CDCl_3$ follow: **2R$_1$**, δ 2.80 (3-CH_3), 4.35 (5-CH_3O), 4.10 (7-CH_3O); **2R$_2$**, δ 1.25 (3 H) and 3.10 (2 H) in 3-ethyl, 4.30 (5-CH_3O), 4.10 (7-CH_3O).

(10) The incident light at 254 nm was absorbed by the solvent (R_3CN) com-

pletely, and the decomposition of **1** sensitized by the singlet excited state of R_3CN would undergo the photocycloaddition to R_3CN.

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(15) Benzophenone concentration in R_1CN was 0.1 *M*. There was no uv absorption band of **1** in wavelengths longer than 310 nm.

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N-Dealkylation of Pyrazoles Using Pyridine Hydrochloride

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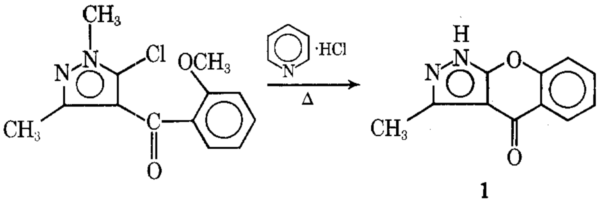
We wish to report that *N*-alkylpyrazoles can be conveniently N-dealkylated by heating in anhydrous pyridine hydrochloride at reflux temperature. We fortuitously observed this N-dealkylation when 5-chloro-1,3-dimethylpyrazol-4-yl-*o*-methoxyphenyl ketone[1] was heated for 16 hr at 215° with this reagent and the product was shown to be 3-methyl[1]benzopyrano[2,3-*c*]pyrazol-4(1*H*)-one (1) (Scheme I).

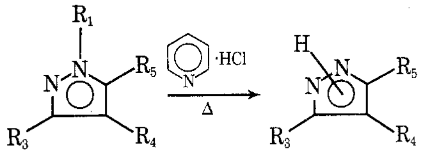
Scheme I



1

There are only a few reports on the removal of N substituents from pyrazoles[2-6] and most of these N substituents are of such low stability as to preclude their use for protective purposes. Thus base and heat have been shown to remove the *N*-hydroxymethyl,[2] N-substituted aminomethyl,[2] and *N*-2,4-dinitrophenyl[3] groups. Also oxidative reagents remove particularly sensitive N-substituents.[4,5] The most synthetically useful N-protecting group in pyrazole chemistry is the *N*-benzyl group[6] (readily removed by sodium and liquid ammonia reduction, but suffering the usual disadvantages associated with this method of removal). Therefore, we decided to test the generality of this N-dealkylation (Scheme II). *N*-Alkylcarboxylic acid amides, anilides,[7] and *N*-methyl- and *N*-ethylphenothiazine[8] have been dealkylated by this reagent. The generality of this reaction has been questioned, since *N*-alkylcarbazoles are unaffected by this reagent.[9]

Scheme II



Results

Both simple and complex *N*-methylpyrazoles as well as *N*-ethylpyrazoles (see compounds **5** and **8**, Table I) and one example of an *N*-methylindazole (see compound **3**) were successfully N-dealkylated. The reaction was successful with a wide variety of substituents on the carbon atoms of the pyrazole ring, including both electron-attracting and -releasing substituents. Wide differences in the rate of N-dealkylations were observed [see time of heating, Table I, and comparison of synthesis of **6** from 1,3-dimethylpyrazol-5-yl phenyl ketone[10] or the isomeric 1,5-dimethylpyrazol-3-yl phenyl ketone (**9**) in Experimental Section]. This is a rapid, simple method and gives reasonably good yields of N-unsubstituted pyrazoles. The examples include a number of compounds that would be difficult or impossible to prepare by other methods. While the examples have included only *N*-methyl and *N*-ethyl substituents, in analogy with the known N,N′-dealkylations of *N,N′*-pyrazolium and *N,N′*-indazolium quaternary salts[11,12] other alkyl groups should be removed with equal facility.

Mechanistic Considerations. The reaction most likely proceeds by protonation of the pyrazole ring and the formation of the alkyl halide by the attack of chloride ion and expulsion of the neutral N-dealkylated pyrazole. The high temperature drives out the low-boiling alkyl halide, helping to drive the reaction to completion. This is consistent with the mechanism in the N,N′-dealkylations of *N,N′*-dialkylpyrazolium halides.[11] Examination of the crude product in the synthesis of **6** demonstrated the presence of an *N*-methyl shift as reported in N,N′-dealkylations of *N*-methyl-*N′*-alkylpyrazolium salts.[11]

Experimental Section[13]

Reagents and Starting Materials. The pyridine was purchased from J. T. Baker Chemical Co. The following compounds were synthesized as described in the references given: 5-chloro-1,3-dialkylpyrazol-4-yl aryl ketones;[1] 1,3-dimethylpyrazol-5-yl phenyl ketone;[10] 1-ethyl-3-methyl-4-nitropyrazol-5-yl phenyl ketone;[14] 1,3,5-trimethylpyrazole;[15] 5-amino-1,3-dimethylpyrazole;[16] 1,5-dimethyl-3-pyrazolecarboxamide;[17] 1,3-dimethyl-1*H*-indazole.[18]

General Procedure. Anhydrous pyridine hydrochloride was freshly prepared by the method of Curphey et al.[19] (dried by distillation up to 210° and cooled under a stream of N_2). The pyrazole was added to a three- to tenfold molar excess of the reagent and the mixture was stirred at 180–218° for 1–40 hr. Products less basic than pyridine could be isolated by dilution of the cooled reaction mixture with water followed by filtration or extraction with diethyl ether or chloroform. The extracts were dried ($MgSO_4$) and concentrated and the products were recrystallized. If the product was a stronger base than pyridine, it was isolated by addition of an excess of 29% ammonia and extraction. Many of the keto pyrazoles were best separated from unreacted starting material by extraction into 1 *N* sodium hydroxide solution followed by neutralization with an equivalent amount of hydrochloric acid.

3-Methylpyrazol-5-yl Phenyl Ketone (6). 1,3-Dimethylpyrazol-5-yl phenyl ketone[10] was treated with the reagent for 1 hr at 218°. A VPC on the crude reaction mixture showed a three-component mixture: starting material (5%), **6** (80%), and an unknown, **9** (15%). Two recrystallizations from toluene yielded **6** (52%) (see Table I for physical data). The unknown **9** was shown to be the