Synthesis and Photolysis of Some Substituted Quinoxaline Di-*N*-oxides[1]

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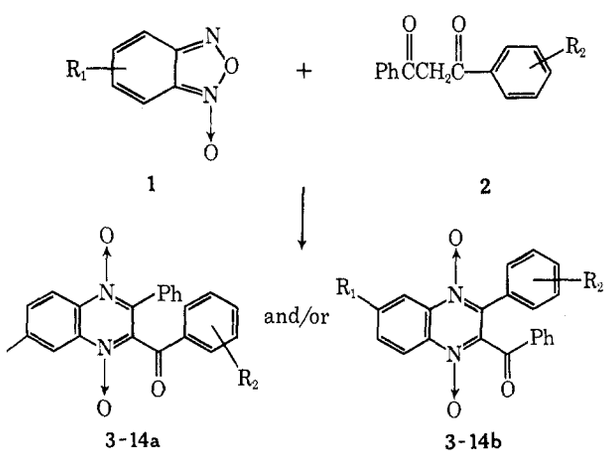
Received July 21, 1970

This paper reports qualitative studies of substituent effects on the scope of the reaction of benzofurazan oxide with aroylacetophenones to form quinoxaline di-*N*-oxides, as well as the photochemical rearrangements of the latter compounds to 1,3-diaroylbenzimidazolones. Mechanistic possibilities for these two transformations are discussed.

In a previous report[2] we have shown that benzofurazan oxide (**1**) reacted with enolate anions to give quinoxaline di-*N*-oxides. For example, benzofurazan oxide (**1**, R_1 = H) reacted with diaroylmethanes (**2**, R_2 = H) in the presence of amines to give 2-phenyl-3-benzoylquinoxaline di-*N*-oxide (**3a,b**, $R_1 = R_2$ = H). With unsymmetrical 1,3 diketones, this reaction could conceivably yield one or two isomeric quinoxaline di-*N*-oxides.

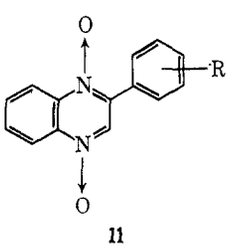


The purpose of this work was twofold: first, to investigate whether ortho or para substituents in 1,3-diaroylmethanes, and/or whether substituents in benzofurazan oxide, would have a directive, effect in controlling the nature of the product(s) of this reaction; second, to study the generality of the photolytic rearrangement of the products of the reaction, namely, 2-aryl-3-aroylquinoxaline di-*N*-oxides, to 1,3-dibenzoylbenzimidazolones.

Synthesis.—The specific substituted aroylacetophenone and benzofurazan oxide were dissolved in warm diethylamine, the solution was allowed to stand at room temperature, and the precipitated product was collected (Table I).

It was found that two isomeric quinoxaline di-*N*-oxides **a** and **b** (**4a,b**; **5a,b**; **6a,b**; **7a,b**) were obtained from *para*-substituted aroylacetophenone **2** (R_2 = *p*-Br, *p*-OCH_3, *p*-CH_3, *p*-NO_2) and benzofurazan oxide, respectively. ortho-Substituted aroylacetophenone **2** (R_2 = *o*-CH_3, *o*-OCH_3) each gave a single product, namely, 2-phenyl-3-(*o*-methylbenzoyl)quinoxaline di-*N*-oxide (**8a**) and 2-phenyl-3-(*o*-methoxybenzoyl)quinoxaline di-*N*-oxide (**9a**), respectively. *o*-Nitrobenzoylacetophenone (**2**, R_2 = *o*-NO_2) yielded (2-*o*-nitrophenyl)-3-benzoylquinoxaline di-*N*-oxide (**10b**) and 2-phenyl-3-(*o*-nitrobenzoyl)quinoxaline di-*N*-oxide (**10a**). Attempts to separate these isomeric mixtures by column chromatography were unsuccessful; integration of the nmr signals of the methyl groups in **5a,b** and of the methoxy groups in **6a,b** indicated that isomers **a** and **b** were formed in about the same amount.

The following experiments support the structural assignments of the above di-*N*-oxides. Cleavage of quinoxaline di-*N*-oxides **8a** and **9a** with methanolic potassium hydroxide yielded 2-phenylquinoxaline di-*N*-oxide (**11**, R = H) as the sole product, the identity of which was established by comparison with an authentic sample.[1] On the other hand, cleavage of the isomeric mixtures of quinoxaline di-*N*-oxides **4a,b**, **5a,b**, **6a,b**, **7a,b**, and **10a,b** with methanolic potassium hydroxide yielded a mixture of **11** (R = H) and 2-phenyl-substituted quinoxaline di-*N*-oxides (**11**, R = *p*-Br, *p*-CH_3, *p*-OCH_3, *p*-NO_2, and *o*-NO_2). These mixtures, after recrystallization, showed a wide range in melting points, and their infrared spectra displayed bands at 800–825 (para-substituted phenyl), and at 760–780 cm^{-1} (ortho-substituted phenyl). The formation of quinoxaline di-*N*-oxides **5a,b** and **6a,b** was confirmed by their nmr spectra. Products **5a,b** showed two peaks at τ 6.26 and 6.34 as expected for two different methoxy groups. Similarly, quinoxaline di-*N*-oxides **6a,b** displayed two peaks for two methyl groups at τ 7.62 and 7.70. The nmr spectra of **8a** and **9b** each exhibited a single band at τ 7.6 and 6.4, respectively.



Additional structural information came from infrared spectra which showed a characteristic band of aromatic *N*-oxides at 1320–1330 cm^{-1}, and nmr spectra which displayed two multiplets centered at τ 1.3 and 2.4, where the τ 1.3 multiplet is consistent with the expected considerable deshielding of the aromatic protons at positions 5 and 8.

From the above findings, it appears that, whereas para substituents in aroylacetophenones have no directive effect that would control the nature of the product, ortho substituents seem to favor the formation of a single product. The selectivity of the latter can be explained by postulating species **15** as an intermediate

(1) Abstracted in part from the M.S. Thesis of Mr. G. Agopian, American University of Beirut, June 1968.

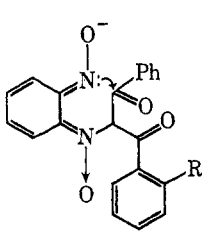
(2) C. H. Issidorides and M. J. Haddadin, *J. Org. Chem.*, **31**, 4067 (1966).

TABLE I[a]

Quinoxaline di-*N*-oxide	R_1	R_2	Mp, °C	% yield	Infrared, cm^{-1}	Nmr, τ (multiplicity)
4a,b	H	*p*-Br	222–224 dec	60	1675, 1585, 1340, 1250, 1090, 900, 875, 805, 765, 680	1.3 (m) 2.36 (m)
5a,b	H	*p*-OCH_3	197–198 dec	47	1670, 1600, 1340, 1250, 1170, 1090, 1025, 900, 875, 760, 680	1.24 (m) 2.64 (m) 6.26 (s) 6.34 (s)
6a,b	H	*p*-CH_3	217–218 dec	54	1670, 1600, 1335, 1240, 1090, 900, 870, 800, 760, 690	1.36 (m) 2.36 (m) 7.62 (s) 7.70 (s)
7a,b	H	*p*-NO_2	204–205 dec	62	1680, 1600, 1580, 1520, 1345, 1280, 1235, 1090, 1000, 905, 870, 770, 725, 690	1.32 (m) 2.20 (m)
8a	H	*o*-CH_3	223–225 dec	52	1670, 1600, 1510, 1345, 1220, 1090, 1000, 890, 877, 780, 750, 700, 670	1.32 (m) 2.60 (m) 7.60 (s)
9a	H	*o*-OCH_3	217–218 dec	40	1650, 1600, 1518, 1345, 1250, 1160, 1010, 900, 875, 760, 710, 665	1.32 (m) 2.60 (m) 6.40 (s)
10a,b	H	*o*-NO_2	127–129 dec	57	1675, 1600, 1525, 1340, 1170, 1075, 880, 850, 790, 705, 690	1.32 (m) 2.32 (m)
11a,b	CH_3	H	220–228	34	1675, 1335, 1100, 888, 845, 820, 775, 740, 700	1.6 (m) 2.2 (m) 2.6 (m) 7.4 (s)
12a,b	OCH_3	H	221–224	36	1670, 1610, 1595, 1330, 1245, 900, 885, 770, 710, 700, 655	1.4 (d) 2.2 (m) 2.8 (s) 6.0 (s)
13a,b	Cl	H	211–216	31	1680, 1590, 1580, 1400, 1335, 1310, 1230, 1100, 890, 840, 760, 700, 670	1.4 (m) 2.8 (m) 2.6 (m)
14	6,7-Dimethyl	H	240–242	46	1675, 1335, 1180, 1160, 893, 830, 740, 690	1.56 (s) 1.64 (s) 2.6 (m) 7.5 (s)

[a] Satisfactory analytical values (±0.4% for C, H, and N) were reported for all compounds, and mixtures of isomers, in the table except for the mixture of **7a,b** (Calcd: C, 65.11. Found: C, 63.10.).

in the reaction. Ring closure in this intermediate is more feasible *via* an attack on the carbonyl group at-



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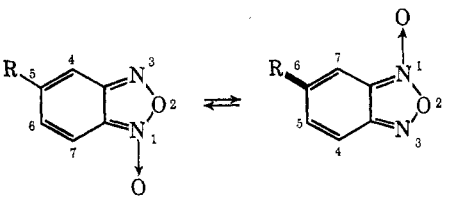
tached to the phenyl group that carries no ortho substituent, a process that entails minimum steric hindrance. Such interaction is absent in the case of para-substituted aroylacetophenones; therefore, no selectivity was observed. The formation of a mixture of **10a** and **10b** from **2** (R_2 = *o*-NO_2) is not easy to explain; yet it is plausible that the inductive effect of the *o*-nitro group activates the neighboring carbonyl group to an extent that this effect counterbalances the steric effect.

The reaction of substituted benzofurazan oxide with 1,3-dibenzoylmethane could give rise to one or two quinoxaline di-*N*-oxides. Two obvious factors might contribute to the determination of the nature of the product(s). First, the structure of the substituted benzofurazan oxide. It has been shown by Katritzky,[3] *et al.*, that tautomerism in substituted benzofurazan oxides is rather facile. Nmr evidence indicated that electron-acceptor groups favored the 6 position, and electron-donor groups the 5 position (**16**). It is clear



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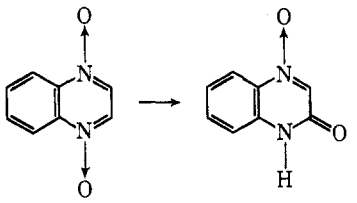
(3) A. R. Katritzky, S. Øksne, and R. K. Harris, *Chem. Ind. (London)*, 990 (1961); A. J. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, *J. Chem. Soc. B*, 914 (1967).

that a reaction of substituted benzofurazan oxide could involve either or both tautomers. Assuming that a substituted benzofurazan oxide reacted with 1,3-dibenzoylmethane by a single mode of reaction (see below), two quinoxaline di-*N*-oxides would result if both tautomers took part in the reaction and one product would be obtained if only one tautomer reacted.

The second factor involves the mode by which the enolate anion attacks the substituted benzofurazan oxide. Essentially, the question is whether the enolate anion attacks nitrogen 1 or/and nitrogen 3 (the latter mode of attack is analogous to a 1,4-addition reaction). Although a specific attack on nitrogen 1 with a synchronous cleavage of the N_1–O_2 bond would result in a relief of strain in the five-membered ring, the mechanism of this reaction is not discernible at this point. The ease of cleavage of the N_1–O_2 bond is apparent from the facile tautomerism of benzofurazan oxides.

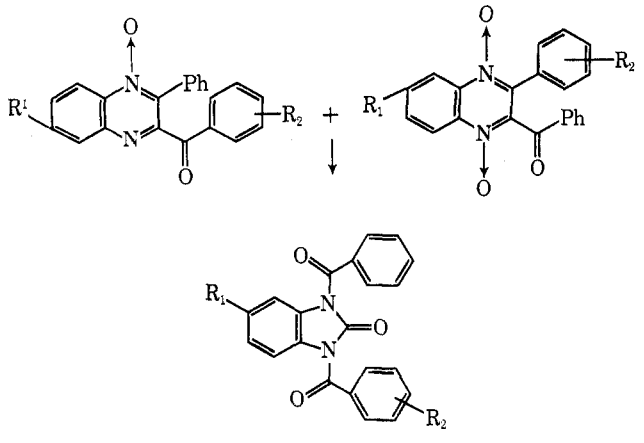
The reaction of 5(6)-substituted benzofurazan oxide (**1**, R_1 = CH_3, OCH_3, Cl) with 1,3-dibenzoylmethane resulted in the formation of quinoxaline di-*N*-oxides **11a,b**, **12a,b**, and **13a,b** which, after recrystallization, melted over a range of temperature and therefore indicated the formation of a mixture of the possible isomers **a** and **b**. 5,6-Dimethylbenzofurazan oxide gave 2-phenyl-3-benzoyl-6,7-dimethylquinoxaline di-*N*-oxide (**14**). The structures of the above products were established by elemental analysis and spectroscopic data (see Table I).

Photolysis.—The photochemical reactions of aromatic amine oxides have recently been the subject of intensive investigations.[4a] Little is known about the photochemical reactions of quinoxaline di-*N*-oxides. Landquist[4b] briefly reported the photolysis of quinoxaline di-*N*-oxide (**27**) to yield 2-quinoxalone 4-*N*-oxide (**28**).



27 **28**

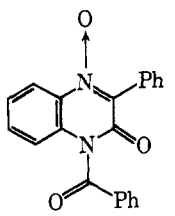
We have shown that 2-phenyl-3-benzoylquinoxaline di-*N*-oxide, when irradiated in methanol, rearranged



into 1,3-dibenzoylbenzimidazolone in good yield.[5] In this study, the generality of this novel rearrangement was examined. The irradiation of 2-aryl-3-aroylquinoxaline di-*N*-oxides **4a,b**, **5a,b**, **6a,b**, **7a,b**, **8a,b**, **9a**, **11a,b**, **12a,b**, **13a,b**, and **14** in methanol yielded the corresponding 1,3-diaroylbenzimidazolones listed in Table II (**17**–**26**).

The progress of the reaction was monitored by thin layer chromatography. The yields were fair to good. Quinoxaline di-*N*-oxides **10a** and **10b** did not give the corresponding benzimidazolone and, instead, decomposed into an intractable tarry material. The decomposition of these reactants could probably be due to the intramolecular interaction of ortho nitrochromophore with the carbonyl group.[6]

The mechanism proposed for the above rearrangement[5] involved **29** as an intermediate.



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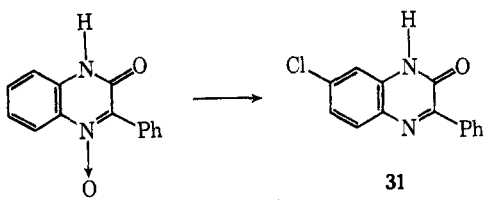
In one unsuccessful attempt to prepare **29**, 3-phenyl-2(1*H*)-quinoxalone 4-oxide[7] (**30**) was treated with benzoyl chloride in pyridine. This reaction did not yield **29** but gave 3-phenyl-7-chloro-2(1*H*)-quinoxalonone (**31**) in high yield. This transformation is analogous to that reported by Ahmad, *et al.*[8] Other approaches to the synthesis of **29** are in progress. The elusiveness of **29** to synthesis is not surprising in the light of the recent findings of Curtin and Englemann who have shown that the O- or N-benzoylation of 5(6*H*)-phenanthrolinone are effected under strict conditions.[9]



30 **31**

In conclusion, it was shown that para substituents in aroylacetophenones and monosubstituents in benzofurazan oxides have no directive effect on the resulting quinoxaline di-*N*-oxides, while ortho substituents in aroylacetophenones do have such an effect. The photolysis of a number of 2-aryl-3-aroylquinoxaline di-*N*-oxides to yield unsymmetrical 1,3-diaroylbenzimidazolones was shown to be a general reaction and a simple method for the preparation of 1,3-benzimidazolone derivatives.

(4) (a) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); (b) J. K. Landquist, *J. Chem. Soc.*, 2830 (1953).

(5) M. J. Haddadin and C. H. Issidorides, *Tetrahedron Lett.*, 753 (1967).

(6) G. M. J. Schmidt in "Reactivity of Photoexcited Organic Molecule," Interscience, London, 1967, pp 227–284.

(7) G. Tennant, *J. Chem. Soc.*, 2666 (1964).

(8) Y. Ahmad, M. S. Habib, Ziauddin, and N. Bashir, *Bull. Chem. Soc. Jap.*, **38**, 1654 (1965).

(9) D. Y. Curtin and J. H. Engelmann, *Tetrahedron Lett.*, 3911 (1968).

TABLE II[a]

Quinoxaline di-*N*-oxide	Photolysis time	Diaroylbenzimidazolone	R_1	R_2	Mp, °C	% yield	Infrared, cm^{-1}
4a,b	45 min	**17**	H	*p*-Br	225	50	1743, 1700, 1335, 1160, 1050, 845, 753, 720, 700
5a,b	1 hr	**18**	H	*p*-CH_3	214	55	1740, 1693, 1600, 1330, 1300, 1255, 1160, 1050, 1030, 910, 850, 760, 720, 675
6a,b	45 min	**19**	H	*p*-OCH_3	226	40	1750, 1700, 1600, 1520, 1335, 1160, 1050, 865, 830, 775, 700, 667
7a,b	45 min	**20**	H	*p*-NO_2	208	20	1750, 1700, 1600, 1520, 1335, 1160, 1050, 865, 830, 775, 700, 667
8a	2 hr	**21**	H	*o*-CH_3	154	40	1745, 1700, 1330, 1160, 1040, 900, 835, 793, 760, 700, 670
9a	1 hr	**22**	H	*o*-OCH_3	211	45	1765, 1680, 1600, 1340, 1250, 1160, 1025, 750, 700, 670
11a,b	2 hr	**23**	CH_3	H	224–225	33	1750, 1700, 1600, 1500, 1320, 1190, 1150, 1050, 1020, 930, 820, 750, 720, 710, 695, 680
12a,b	2 hr	**24**	OCH_3	H	209–211	18	1780, 1690, 1600, 1490, 1320, 1170, 1050, 1020, 860, 840, 800, 750, 720, 700, 670
13a,b	1 hr	**25**	Cl	H	194–196	33	1750, 1700, 1600, 1485, 1320, 1160, 1050, 1020, 910, 820, 790, 750, 700, 615, 610
14	2 hr	**26**	5,6-Dimethyl	H	221–223	25	1755, 1690, 1490, 1320, 1175, 1155, 745, 705, 615

[a] Satisfactory analytical values (±0.25% for C, H, and N) were reported for compounds **17–26** inclusive: Ed.

Experimental Section[10]

All of the 1,3 diketones used in this study were prepared according to reported methods.[11,12]

General Procedure for the Preparation of Quinoxaline Di-*N*-oxides.—A warm solution of benzofurazan oxide and the specific 1,3 diketone in diethylamine was left to stand at room temperature for a time that varied between 2 and 3 days. The precipitated products were collected, washed with ethanol, and dried. Recrystallization from ethanol yielded yellow crystalline quinoxaline di-*N*-oxides. It should be pointed out that the melting points of quinoxaline di-*N*-oxides depend on the rate of heating, and hence are not good criteria for purity.

General Procedure for the Photolysis of Quinoxaline Di-*N*-oxides.—A solution of the specific quinoxaline di-*N*-oxide (0.5–1.0 g) in either methanol or ethanol was irradiated by a Hanovia 450-W ultraviolet lamp. On concentration of the solution (25–50 ml), the precipitated product was collected and recrystallized from ethanol. Physical and spectroscopic properties of the quinoxaline di-*N*-oxides and their photolysis products are listed in Tables I and II.

Conversion of 3-Phenyl-2(1*H*)-quinoxalone 4-Oxide (30) into 3-Phenyl-7-chloro-2(1*H*)-quinoxalone (31).—A solution of 3-phenyl-2(1*H*)-quinoxalone 4-oxide[7] (2.4 g) in pyridine (100 ml) and benzoyl chloride (1.5 g) was refluxed for 30 min. The cold solution was diluted with water and the resulting solid was collected, washed with water–ethanol, and dried. Recrystallization from ethanol gave 2.1 g of 3-phenyl-7-chloro-2(1*H*)quinoxalone (**31**) as pale yellow needles, mp 277–278° (lit.[8] mp 274–275°).

Cleavage of Quinoxaline Di-*N*-oxides with Base.—A suspension of the specific quinoxaline di-*N*-oxide (0.1–0.2 g) in 5% methanolic potassium hydroxide (20 ml) was heated until the solid dissolved. The yellow precipitate (0.07–0.15 g), obtained on cooling, was collected and recrystallized from ethanol. See Table III.

TABLE III

Quinoxaline di-*N*-oxide	Cleavage product(s)
4a,b	2-Phenylquinoxaline di-*N*-oxide and 2-(*p*-bromophenyl)quinoxaline di-*N*-oxide
5a,b	2-Phenylquinoxaline di-*N*-oxide and 2-(*p*-methoxyphenyl)quinoxaline di-*N*-oxide
6a,b	2-Phenylquinoxaline di-*N*-oxide and 2-(*p*-methylphenyl)quinoxaline di-*N*-oxide
7a,b	2-Phenylquinoxaline di-*N*-oxide and 2-(*p*-nitrophenyl)quinoxaline di-*N*-oxide
8a	2-Phenylquinoxaline di-*N*-oxide
9a	2-Phenylquinoxaline di-*N*-oxide
10a,b	2-Phenylquinoxaline di-*N*-oxide and 2-(*o*-nitrophenyl)quinoxaline di-*N*-oxide

(10) Melting points are uncorrected. Infrared spectra were taken in Nujol using a Perkin-Elmer grating infrared spectrophotometer Model 257. Nmr spectra were run in deuterated chloroform on a Varian A-60D spectrometer. Elemental analyses were performed by F. Pascher, Bonn, Germany.

(11) F. J. Pond, O. P. Maxwell, and G. M. Norman, *J. Amer. Chem. Soc.*, **21**, 955 (1899).

(12) W. Bradley and R. Robinson, *J. Chem. Soc.*, 2356 (1926).

Registry No.—4a, 27017-72-7; 4b, 27017-73-8; 5a, 27017-74-9; 5b, 27017-75-0; 6a, 27017-76-1; 6b, 27017-77-2; 7a, 27017-78-3; 7b, 27017-79-4; 8a, 27017-80-7; 9a, 27017-81-8; 10a, 27017-82-9; 10b, 27017-83-0; 11a, 27017-84-1; 11b, 27017-85-2; 12a, 27017-86-3; 12b, 27062-07-3; 13a, 27062-08-4; 13b, 27017-87-4; 14, 27017-88-5; 17, 27017-89-6; 18, 27017-90-9; 19, 27017-91-0; 20, 27017-92-1; 21, 27017-93-2; 22, 27017-94-3; 23, 27017-95-4; 24, 27017-96-5; 25, 27017-97-6; 26, 27017-98-7.

Acknowledgment.—We are grateful to Chas. Pfizer & Co., Inc., for a generous grant in support of this work and to Mr. Talal Akashah for his assistance.

The s-Triazolone Ring System as a New *cis*-Azo Dienophile

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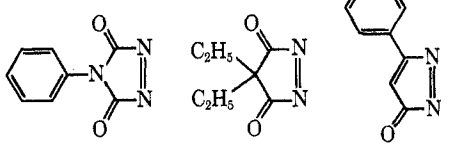
Received June 5, 1970

The oxidation of 5-substituted *s*-triazolin-3-ones (**1a–e**) with lead tetraacetate (LTA) led to the formation of the intermediate *s*-triazolone ring system (**2a–e**) which in the absence of 1,3-dienes decomposed to nitriles plus carbon monoxide and nitrogen. In the presence of 1,3-dienes, 5-aryl-*s*-triazolones (**2a–c**) formed Diels–Alder adducts, the 5,8-dihydro-3-aryl-*s*-triazolo[1,2-*a*]pyridazin-1-one ring system (**3–10**). The oxidation of 5-benzyl- and 5-methyl-*s*-triazolin-3-ones by LTA in the presence of 1,3-dienes did not yield Diels–Alder adducts, and only nitriles and α-phenyldiacetamide and diacetamide, respectively, were isolated.

The reaction of electron-deficient azo compounds with 1,3-dienes has recently been receiving wider attention.[1] Previous workers have investigated the oxidation of five-membered heterocycles *N*-phenylurazole[2,3] (**12**), 4,4-diethylpyrazolidine-3,5-dione[4–6] (**13**), and 3-phenyl-2-pyrazolin-5-one[7] (**14**) with lead tetraacetate (LTA) to give 4-phenyl-1,2,4-triazoline-3,5-dione (**12a**), 4,4-diethylpyrazoline-3,5-dione (**13a**), and 3-phenylpyrazol-5-one (**14a**) which afford Diels–Alder adducts in the presence of 1,3-dienes. The reactivity of **12a** > **13a** > **14a** has been established based on

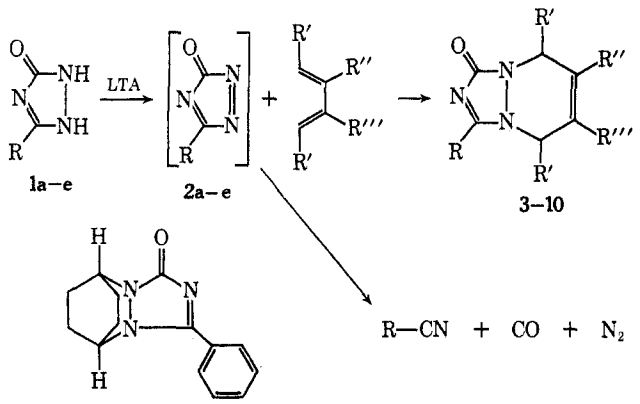


12a **13a** **14a**

the comparison of the number and types of dienes with which adduct formation occurs. These *cis*-azo dienophiles are more reactive than ethyl azodicarboxylate, a *trans*-azo dienophile.[8]

In continuing these investigations, 5-substituted *s*-triazolin-3-ones **1a–e** were oxidized with LTA to give the 5-substituted *s*-triazolones **2a–e**, a new series of *cis*-azo dienophiles as intermediates. Compound **2a** is a 4-aza analog of **14a**. Unlike the oxidations of **12**, **13**, and **14** with LTA, no transient visible color was observed when **1a–e** were treated with LTA. The oxidation products **2a–e** decomposed to nitriles.

The major product of the oxidation of **1a** and **1b** are benzonitrile and *p*-methoxybenzonitrile in 95–99% yield. The oxidation of **1c** with LTA is extremely sluggish. After 1 week of stirring at room temperature only a small quantity of *p*-nitrobenzonitrile was isolated. Isolation of the insoluble materials obtained upon filtration of the reaction mixture afforded unreacted 5-(*p*-nitrophenyl)-*s*-triazolin-3-one (**1c**). This result is consistent with the reduced electron density on the heteroatoms due to the electron-withdrawing *p*-nitro group, thus decreasing the ability of the heterocycle to coordinate with LTA. When **1d** and LTA were allowed to react, phenylacetonitrile was isolated in 75% yield, along with α-phenyldiacetamide which was identified by chemical analysis and infrared and nmr spectroscopy. Saponification of the amide afforded phenylacetic acid. Formation of the amide may be rationalized by either the formation of an azoacetate (A) which may then decompose to B followed by decomposition to the nitrile. Azoacetate A may



Compounds	R	R′	R″	R‴
1a, 2a, 3	Phenyl	H	H	CH_3
1a, 2a, 4	Phenyl	H	CH_3	CH_3
1a, 2a, 5	Phenyl	Phenyl	H	H
1a, 2a, 6	Phenyl	CH_2	H	H
1b, 2b, 7	*p*-Methoxyphenyl	H	CH_3	CH_3
1b, 2b, 8	*p*-Methoxyphenyl	Phenyl	H	H
1b, 2b, 9	*p*-Methoxyphenyl	CH_2	H	H
1c, 2c, 10	*p*-Nitrophenyl	H	CH_3	CH_3
1d, 2d,	Benzyl			
1e, 2e,	Methyl			

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