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.

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

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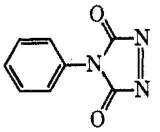
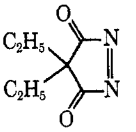
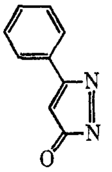
The oxidation of 5-substituted *s*-triazolin-3-ones (**1a–e**) with lead tetraacetate (LTA) led to the formation of the intermediate *s*-triazolone ring system (**2a–e**) which in the absence of 1,3-dienes decomposed to nitriles plus carbon monoxide and nitrogen. In the presence of 1,3-dienes, 5-aryl-*s*-triazolones (**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.

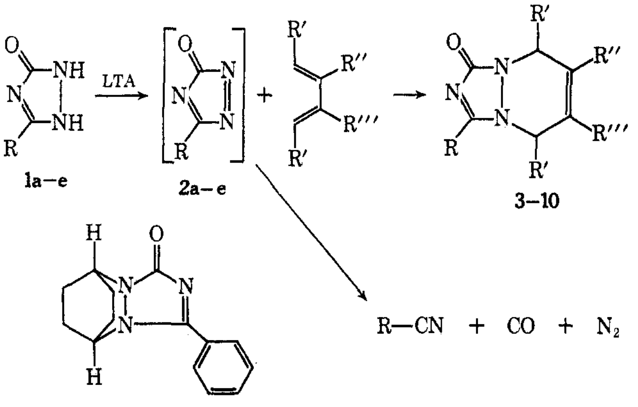
The reaction of electron-deficient azo compounds with 1,3-dienes has recently been receiving wider attention.[1] Previous workers have investigated the oxidation of five-membered heterocycles *N*-phenylurazole[2,3] (**12**), 4,4-diethylpyrazolidine-3,5-dione[4–6] (**13**), and 3-phenyl-2-pyrazolin-5-one[7] (**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 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]


12a


13a


14a

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.



1a–e **2a–e** **3–10** **11**

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			

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

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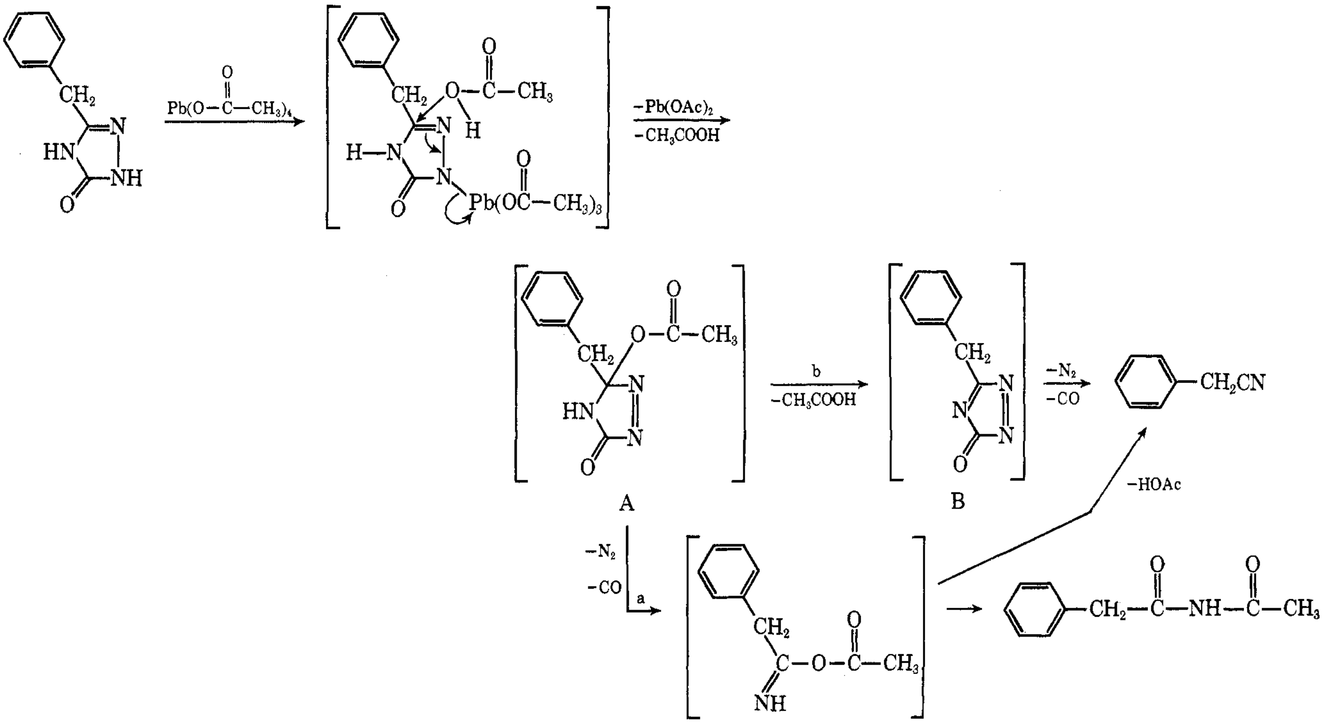
Scheme I



also decompose *via* pathway a which may lead to α-phenyldiacetamide. When **1e** and LTA were allowed to react, acetonitrile and diacetamide were obtained. Their formation may be rationalized by the proposed pathway shown in Scheme I. In the presence of 1,3-dienes, intermediates **2a**, **2b**, and **2c** were trapped before complete decomposition to yield new Diels–Alder adducts, the 5,8-dihydro-3-aryl-*s*-triazolo[1,2-*a*]pyridazin-1-one ring system (**3**–**10**).

Thus, when **1a** was oxidized with LTA in the presence of 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,4-diphenyl-1,3-butadiene, and 1,3-cyclohexadiene, Diels–Alder adducts **3**, **4**, **5**, and **6** were obtained, respectively. Diels–Alder adducts **7**, **8**, and **9** were obtained when **1b** was oxidized by LTA in the presence of 2,3-dimethyl-1,3-butadiene, 1,4-diphenyl-1,3-butadiene, and 1,3-cyclohexadiene. The oxidation of **1c** by LTA in the presence of 2,3-dimethyl-1,3-butadiene afforded **10** in low yield owing to the decreased reactivity of the heterocycle toward oxidation, and most of the LTA was utilized in the oxidation of the diene. Higher yields of adducts **3**–**10** were obtained when the reaction was carried out at ambient temperatures rather than at 0–5°. At 0–5° the reaction required 24 hr for completion, while at −40 or −70° the reaction required longer than 72 hr. No adduct was obtained from **1a** and 1,3-cyclopentadiene; this is not surprising in view of the low reactivity of the 5-aryl-*s*-triazolin-3-one ring system toward LTA and the high reactivity of 1,3-cyclopentadiene. Even at −10° or below oxidation of the diene was rapid.[12] When **1d** or **1e** was oxidized by LTA in the presence of 1,3-dienes, no Diels–Alder adducts were obtained and only decomposition products were isolated. This may be due to the formation of the azoacetate A which is not a reactive dienophile. Decomposition *via* pathway a affords an imino ester which may also decompose to give the nitrile and the amide.

The infrared spectra of the 5-aryl-*s*-triazolin-3-ones **1a**, **1b**, and **1c** exhibited a C=O stretch at 1754, 1724, and 1680 cm^{-1}, respectively. These values are in agreement with the structures indicated by **1a–c**.[9] A band of medium intensity was exhibited by **1a**, **1b**, and **1c** at 971 cm^{-1} (N—N stretch)[10] which was absent in the adducts **3**–**9**. The C=O stretch in the adducts **3**–**6**, **7**–**8**, and **9** appeared at 1681, 1667, and 1651 cm^{-1}, respectively.

The nmr spectra of the adducts **4** and **8** exhibited nonequivalence of the methylene protons due to the different adjacent environments of each of the two nitrogen atoms. In adducts **6** and **9** nonequivalent methine protons were also observed. An A_2B_2 splitting pattern to adducts **6** and **9** was observed due to the different magnetic environments of the hydrogens of the 5,8-ethano group. Upon hydrogenation of **6** to **11**, the A_2B_2 pattern coalesced to one peak while the methine protons underwent a large shift in position. The shift of the λ_{max} in the ultraviolet spectrum of **6** to shorter wavelength in **11** is indicative of a transannular interaction similar to that reported by Weinkam.[7] The assignment of **3** from isoprene and **2a** is arbitrary since no conclusive evidence has been found to indicate a preferred structure.

The reaction of **1a**, LTA, and 2,5-dimethyl-2,4-hexadiene afforded a new compound, **15a**, which was found to be similar to **16** isolated by Hagarty[3] and is not related to **17** isolated by Weinkam.[7] That the structure is **15a** and not **15b** is based on the observation that the anions of the *s*-triazolin-3-ones absorb at longer wavelengths in the ultraviolet spectrum than the neutral substances, except in the case of a 2-sub-

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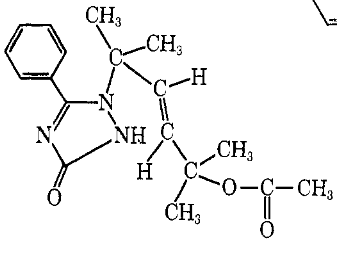
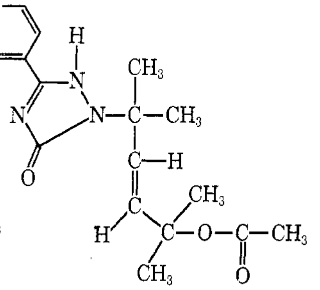
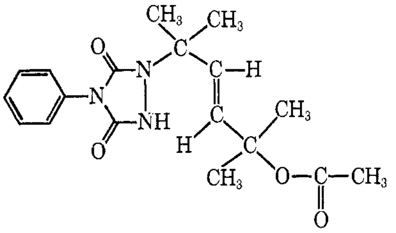
stituted *s*-triazolin-3-one which undergoes a shift to shorter wavelength.[11]



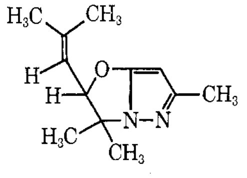
15a



15b



16



17

The difference in reactivity of 5-phenyl-*s*-triazolin-3-one (**1a**) and that of 3-phenyl-2-pyrazoline-5-one (**14**)[7] toward LTA is to be noted. In spite of the name given for **14** the infrared spectrum reveals a strong hydrogen bonding absorption between 3300 and 2000 cm^{-1} and absence of C=O absorption, and the compound exists as the hydroxy tautomer.[12] The infrared spectrum of **1a** reveals a C=O stretch typical of a carbonyl system in the five-membered ring. There is little evidence to indicate the presence of a hydroxy tautomer in the solid state. Polya[11] found that 1-phenyl-*s*-triazolin-3-one has a similar λ_{max} in the ultraviolet spectrum as does 1-phenyl-2-methyl-*s*-triazolin-3-one and concluded that the lactam formed in the monosubstituted *s*-triazolin-3-ones is more important. The infrared spectra of 4,4-diethyl-pyrazolidine-3,5-dione,[13] maleic hydrazide,[14] and phthalazinedione[15] reveal a C=O stretch typical for their ring size, but there is also a considerable amount of hydrogen bonding exhibited, indicating the presence of the hydroxy tautomer. These cyclic hydrazides are readily oxidized by LTA and the oxidation products are potent *cis*-azo dienophiles. Based on this evidence it appears that the presence of the hydroxy tautomer is important for the rapid oxidation of a cyclic hydrazide.

Thus the oxidation by LTA of the readily available 5-aryl-*s*-triazolin-3-ones affords a facile route to the previously unreported 5,8-dihydro-3-aryl-*s*-triazolo[1,2-*a*]pyridazin-1-one ring system.

Experimental Section[16]

The 5-substituted *s*-triazolin-3-ones **1a,b,d,e** were prepared by the cyclization of acylsemicarbazides[17] and **1c** was prepared by the reaction of *p*-nitrobenzonitrile with semicarbazide.[18] Acylsemicarbazides are readily available from the reaction of acylhydrazides and potassium cyanate in dilute hydrochloric acid or dilute acetic acid.[17]

Oxidation of 5-Substituted *s*-Triazolin-3-ones with LTA. General Procedure.—To a stirred slurry of 8 g (0.05 mol) of 5-phenyl-*s*-triazolin-3-one (**1a**) or 4.8 g (0.025 mol) of 5-(*p*-methoxyphenyl)-*s*-triazolin-3-one (**1b**) or 5.2 g (0.025 mol) of 5-(*p*-nitrophenyl)-*s*-triazolin-3-one (**1c**) or 8.8 g (0.05 mol) of 5-benzyl-*s*-triazolin-3-one (**1d**) was added an equivalent mole quantity of LTA dissolved in 150 ml of dry methylene chloride over a period of 0.5 hr at room temperature. An equivalent mole quantity of solid LTA was added to a slurry of 5-methyl *s*-triazolin-3-one (**1e**) in 75 ml of dry chlorobenzene. Stirring was continued in all cases until 1 drop of the reaction mixture when added to 5 drops of water no longer gave a precipitate of lead oxide. The reaction mixture of **1a**, **1b**, **1c**, or **1d** was filtered and the organic phase was washed with 100 ml of water, separated, and then washed with 100 ml of 10% potassium carbonate solution. The organic phase was then collected and dried over anhydrous magnesium sulfate and evaporated to yield the products indicated below. The reaction mixture of **1e** was distilled at atmosphere pressure. Collection of the distillate was terminated when the flask temperature reached 100°.

From **1a** was obtained 4.4 ml (94% yield) of crude benzonitrile. The crude product was dissolved in 100 ml of petroleum ether (low boiling), adsorbents were added, and the solution was filtered. The clear filtrate was evaporated to give benzonitrile, $n^{25}\text{D}$ 1.5230 (lit.[19] $n^{25}\text{D}$ 1.5298).

From **1b** was obtained 3.2 g (97% yield) of *p*-methoxybenzonitrile: mp 55–60° (lit.[20] mp 60–61°); ir (Nujol) 2200 (CN), 1250 cm^{-1} (C–O–C).

The reaction mixture from **1c** was stirred for 1 week at room temperature after which time the reaction was still incomplete as evidenced by the appearance of lead oxide when 1 drop of the reaction mixture was added to 5 drops of water. Filtration of the solid afforded a mixture of starting material and lead salts. The solid was extracted with 2 l. of concentrated ammonia–water. Heating of the ammonia–water extracts to remove the ammonia afforded 4 g of starting material **1c**. The filtrate of methylene chloride was treated as previously described which gave a copious precipitate of lead oxide which was removed by filtration. The methylene chloride solution was evaporated to yield 0.2 g of *p*-nitrobenzonitrile: mp 147–149° (recrystallized from acetic acid–water) (lit.[20] mp 148–149°); ir (Nujol) 2220 cm^{-1} (CN).

From **1d** 4.9 g of a liquid was isolated which, upon standing at room temperature for 24 hr, afforded a precipitate. The precipitate was collected and washed with cold diethyl ether. The filtrate and all the ether washings were combined and evaporated to give 2.4 ml of a liquid which was demonstrated to be phenylacetonitrile by comparison of its infrared spectrum with that of authentic phenylacetonitrile, $n^{20}\text{D}$ 1.5120 (lit.[21] $n^{20}\text{D}$ 1.5240).

The solid material was determined to be α-phenyldiacetamide: mp 127–130° (lit.[22] 129–130°); ir (Nujol) 3260, 3165 (NH), 1720 cm^{-1} (C=O); nmr δ 9.5 (s, 1, NH), 7.3 (s, 5, Ar H), 3.8 (s, 2, CH_2), and 2.3 (s, 3, CH_3).

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[16] Melting points are corrected. Microanalyses were performed by Dr. Alfred Bernhardt, Mülheim, Germany. Infrared spectra were taken with a Perkin-Elmer Model 137 double-beam spectrophotometer. The nmr spectra were taken with a Varian Model A-60 using deuteriochloroform as a solvent and tetramethylsilane as an internal reference standard. The ultraviolet spectra were taken with a Cary Model 14 spectrophotometer.

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Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.21; N, 7.91. Found: C, 67.68; H, 6.08; N, 8.07.

Saponification of the product afforded phenylacetic acid, mp 77° (lit.[23] mp 76°).

The infrared spectrum and qualitative tests of the distillate from **1e** revealed the presence of a nitrile, halogenated aromatic hydrocarbon, and acetic acid. The infrared spectrum of the distillate was identical with the infrared spectrum of a sample of the distillate to which authentic acetonitrile was added. Enhancement of the nitrile band was observed and no new bands in the infrared spectrum were observed. Filtration of the solids in the reaction vessel followed by evaporation afforded an oil from which diacetamide slowly crystallized: ir (Nujol) 3448, 3226 (NH), 1754–1667 cm^{-1} (C=O); mp 72–75° (lit.[24] mp 76°).

Reaction of 5-Substituted *s*-Triazolin-3-ones with LTA in the Presence of 1,3-Dienes. General Procedure.—To a stirred slurry of 0.025 mol of 5-substituted *s*-triazolin-3-one and 0.025 mol of 1,3-diene in 100 ml of dry methylene chloride was added 11 g (0.023 mol) of LTA (94% purity) or other molar ratio as indicated, over a period of 30 min at room temperature. The reaction mixture was treated as previously described when 1 drop of the reaction mixture no longer gave a precipitate of lead oxide when added to 5 drops of water. Upon evaporation of the solvent, the solid adducts were obtained. The crude product was washed with 20 ml of diethyl ether to remove unreacted 1,3-diene, nitrile, and acetoxylated materials and the product was then collected on the Büchner funnel and air-dried. The product (1 g) was recrystallized from benzene or methanol to a constant melting point.

5,8-Dihydro-3-phenyl-6-methyl-*s*-triazolo[1,2-*a*]pyridazin-1-one (3).—From a mixture of 8 g (0.05 mol) of **1a** and 5 ml (0.05 mol) of isoprene and 23.5 g (0.027 mol) of LTA was obtained 2.6 g (25%) of **3**: mp 203–205° (benzene); uv λ_{max} (95% ethanol) sh 276 mμ (ϵ 5470) and 237 (12,650); nmr ($DCCl_3$) δ 7.5 (m, 5, Ar H), 5.75 (s, 1, vinyl H), 3.3 (s, 4, $NCH_2C=$), and 1.8 (s, 3, $CH_3C=$).

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.76; N, 18.49. Found: C, 68.60; H, 5.93; N, 18.62.

5,8-Dihydro-3-phenyl-6,7-dimethyl-*s*-triazolo[1,2-*a*]pyridazin-1-one (4).—From a mixture of 4 g of **1a** and 3.1 ml of 2,3-dimethyl-1,3-butadiene and LTA was obtained 3 g (50%) of **4**: mp 198–200° (benzene); uv λ_{max} (95% ethanol) sh 276 mμ (ϵ 5390) and 237 (12,400); nmr ($DCCl_3$) δ 7.5 (m, 5, Ar H), 4.4 (bs, 2, $NCH_2C=$), 4.2 (bs, 2, $NCH_2C=$), and 1.9 (s, 6, $CH_3C=CCH_3$).

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.68; H, 6.28; N, 17.42. Found: C, 69.56; H, 6.12; N, 17.22.

5,8-Dihydro-3,5,8-triphenyl-*s*-triazolo[1,2-*a*]pyridazin-1-one (5).—From a mixture of 4 g of **1a** and 5.2 g of 1,4-diphenyl-1,3-butadiene and LTA was obtained 3.9 g (38%) of **5**: mp 248–250° (methanol); uv λ_{max} (95% ethanol) 285 mμ (ϵ 4670) and 245 (11,700).

Anal. Calcd for $C_{24}H_{19}N_3O$: C, 78.78; H, 5.25; N, 11.50. Found: C, 78.66; H, 5.27; N, 11.57.

5,8-Dihydro-3-phenyl-5,8-ethano-*s*-triazolo[1,2-*a*]pyridazin-1-one (6).—From a mixture of 4 g of **1a** and 2.5 ml of 1,3-cyclohexadiene and LTA was obtained 4 g (66%) of **6**: mp 201–203° (benzene); uv λ_{max} (95% ethanol) 280 mμ (ϵ 5924) and 235 (12,950); nmr ($DCCl_3$) δ 7.85–7.32 (m, 5, Ar H), 6.6–6.19 (m, 2, vinyl H), 5.16 (s, 1, methine CH), 5.10 (s, 1, methine CH), and 2.39–1.62 (AB quartet with δ_A 2.3, δ_B 1.6, J_{AB} = 10 Hz, 4, CH_2CH_2).

Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.39; H, 5.34; N, 17.70.

5,8-Dihydro-3-(*p*-methoxyphenyl)-6,7-dimethyl-*s*-triazolo[1,2-*a*]pyridazin-1-one (7).—From a mixture of 4.8 g of **1b** and 3.1 ml of 2,3-dimethyl-1,3-butadiene and LTA was obtained 2.8 g (38%) of **7**: mp 227–230° (benzene); uv λ_{max} (95% ethanol) 263 mμ (ϵ 16,200); nmr ($DCCl_3$) δ 7.75–6.86 (AB quartet with δ_A 7.7, δ_B 7.0, J_{AB} = 9 Hz, 4, Ar H), 4.26 (bs, 2, $NCH_2C=$), 4.15 (bs, 2, $NCH_2C=$), 3.8 (s, 3, CH_3O), and 1.75 (s, 6, $CH_3C=CCH_3$).

Anal. Calcd for $C_{15}H_{17}N_3O_2$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.25; H, 6.46; N, 15.45.

5,8-Dihydro-3-(*p*-methoxyphenyl)-5,8-diphenyl-*s*-triazolo[1,2-*a*]pyridazin-1-one (8).—From a mixture of 4.8 g of **1b** and 5.2 g of 1,4-diphenyl-1,3-butadiene and LTA was obtained 3 g (30%) of **8**: mp 253–255° (methanol); uv λ_{max} (95% ethanol) 265 mμ (ϵ 16,750); nmr ($DCCl_3$) δ 7.55–6.8 (m, 14, Ar H), 6.16 (d, 2, benzylic CH), 5.8 (m, 2, vinyl H), and 3.8 (s, 3, CH_3O).

Anal. Calcd for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63. Found: C, 75.73; H, 5.32; N, 10.81.

5,8-Dihydro-3-(*p*-methoxyphenyl)-5,8-ethano-*s*-triazolo[1,2-*a*]-pyridazin-1-one (9).—From a mixture of 4.8 g of **1b** and 2.5 ml of 1,3-cyclohexadiene and LTA was obtained 4.5 g (67%) of **9**: mp 185–187° (benzene); uv λ_{max} (95% ethanol) 265 mμ (ϵ 15,100); nmr ($DCCl_3$) δ 7.8–6.9 (AB quartet with δ_A 7.7, δ_B 7.0, J_{AB} = 9 Hz, 4, Ar H), 5.1 (s, 1, methine CH), 5.05 (s, 1, methine CH), 6.5–6.1 (m, 2, vinyl H), 3.85 (s, 3, CH_3O), and 2.36–1.6 (AB quartet with δ_A 2.35, δ_B 1.64, J_{AB} = 10 Hz, 4, CH_2CH_2).

Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61; N, 15.60. Found: C, 67.06; H, 5.78; N, 15.41.

5,8-Dihydro-3-(*p*-nitrophenyl)-6,7-dimethyl-*s*-triazolo[1,2-*a*]-pyridazin-1-one (10).—From a mixture of 5.2 g of **1c** and 3.1 ml of 2,3-dimethyl-1,3-butadiene and LTA was obtained 0.2 g (3%) of **10**: mp 269° dec (methanol); uv λ_{max} (95% ethanol) 260 mμ (ϵ 14,100).

Anal. Calcd for $C_{14}H_{14}N_4O_3$: C, 58.73; H, 4.93; N, 19.57. Found: C, 58.56; H, 4.98; N, 19.40.

5,6,7,8-Tetrahydro-3-phenyl-5,8-ethano-*s*-triazolo[1,2-*a*]pyridazin-1-one (11).—To a slurry of 0.1 g of 5% palladium-on-carbon catalyst in 25 ml of 95% ethanol was added a solution of 2 g (0.0084 mol) of **6** in 60 ml of 95% ethanol. The slurry was stirred under hydrogen at 1 atm a 25° until the theoretical amount of hydrogen had been absorbed (1 hr). The catalyst was removed by filtration and the solvent was removed under reduced pressure to give 1.9 g (90%) of **11**. Recrystallization gave pure **11**: mp 247–248° (benzene); uv λ_{max} (95% ethanol) 277 mμ (ϵ 5890) 235 (12,500); nmr ($DCCl_3$) δ 8–7.3 (m, 5, Ar H), 5.8 (s, 1, methine CH), 4.7 (s, 1, methine CH), and 1.98 (s, 8, CH_2CH_2).

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.68; H, 6.28; N, 17.42. Found: C, 69.53; H, 6.38; N, 17.22.

Reactions of 5-Phenyl-*s*-triazolin-3-one (1a) with Other 1,3-Dienes.—From a mixture of 8 g (0.05 mol) of **1a** and 7.9 ml of 2,5-dimethyl-2,4-hexadiene and 23.5 g of LTA was obtained 8 g (55%) of **15a**: mp 101–103° (50% methanol–water); uv λ_{max} (95% ethanol) 272 mμ (ϵ 14,900); uv λ_{max} (0.1 *N* NaOH in 95% ethanol) 282 mμ (ϵ 8470); nmr ($DCCl_3$) δ 13.5 (s, 1, NH), 8–7.4 (m, 5, Ar H), 6.25 (s, 1, vinyl H), 6.12 (s, 1, vinyl H), 2.08 (s, 3, CH_3), 1.88 (s, 6, CH_3), and 1.75 (s, 6, CH_3).

Anal. Calcd for $C_{18}H_{23}N_3O_3$: C, 65.63; H, 7.04; N, 12.76. Found: C, 65.65; H, 7.35; N, 12.93.

From a mixture of **1a** and 1,3-cyclopentadiene at 0–5, −40, and −70°, only **1a** and acetoxylated materials were recovered. No benzonitrile was observed in the infrared spectrum of the materials isolated. With **1a** and 1,3-cyclooctadiene or anthracene, only benzonitrile, oxidized diene, or anthracene were recovered.

Reactions of 5-Benzyl-*s*-triazolin-3-one and 5-Methyl-*s*-triazolin-3-one with 1,3-Dienes.—When 8.8 g (0.05 mol) of **1d**, 6.2 ml of 2,3-dimethyl-1,3-butadiene, and 23 g of LTA were allowed to react, only phenylacetonitrile and α-phenyldiacetamide were isolated. Similar results were obtained with equimolar quantities of **1d**, 1,3-cyclohexadiene, and LTA. With **1e** and 2,3-dimethyl-1,3-butadiene or 1,3-cyclohexadiene, no adducts were obtained from either the organic phase or from the aqueous washings.

Registry No.—**3**, 27192-78-5; **4**, 27192-79-6; **5**, 27192-80-9; **6**, 27192-81-0; **7**, 27248-71-1; **8**, 27192-82-1; **9**, 27192-83-2; **10**, 27192-84-3; **11**, 27192-85-4; **15a**, 27248-72-2.

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