solution of the ylide prepared from 1-methoxycarbonylmethyl-3-methylbenzimidazolium bromide (**5c**) (3 mmol) and K_2CO_3 (3 mmol) in dimethylformamide (50 ml), dimethyl acetylenedicarboxylate (6 mmol) was added at room temperature and the mixture was stirred for 3 days. The black reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was extracted with acetone and the extract was evaporated to obtain 5-methyl-3,4-bis(methoxycarbonyl)-1-oxo-1,5(2*H*)-pyrido[1,2-*a*]benzimidazole (**10a**) in 6% yield as white prisms: mp 255° (EtOH); ir (KBr) 1740, 1710 ($COOCH_3$), 1655 cm^{-1} (CO); uv λ_{max}^{EtOH} 243 nm (log ϵ 4.23), 314 (3.71), 328 (3.62); nmr δ 3.64 (singlet, NCH_3), 3.91, 4.04 [singlet, $(COOCH_3)_2$], 7.42 (singlet, 3-H), 7.50 (multiplet, aromatic protons), 8.21 (doublet, 6-H); mass spectrum *m/e* 314 (M^+). *Anal.* Calcd for $C_{16}H_{14}N_2O_5$: C, H, N.

Chromatography of the acetone-insoluble part of **10a** on silica gel afforded 1,2,3-tris(methoxycarbonyl)-4-methyl-4*H*-pyrrolo[1,2-*a*]benzimidazole (**9a**) in 7% yield as white prisms: mp 177–178° (EtOH); ir (KBr) 1742, 1690, 1655 cm^{-1} ($COOCH_3$); uv λ_{max}^{EtOH} 247 nm (log ϵ 4 49), 292 (4.29), 331 (4.22); nmr δ 3.86, 3.93, 4.00 [singlet, $(COOCH_3)_3$], 4.23 (singlet, NCH_3), 7.36 (multiplet, aromatic protons), 3.40 (doublet, 8-H); mass spectrum *m/e* 344 (M^+). *Anal.* Calcd for $C_{17}H_{16}N_2O_6$: C, H, N.

Reaction of 3-Ethyl-1-methoxycarbonylmethylbenzimidazolium Ylide with Dimethyl Acetylenedicarboxylate.—A similar reaction occurred with the *N*-ethyl compound. 5-Methyl-3,4-bis(methoxycarbonyl)-1-oxo-1,5(2*H*)-pyrido[1,2-*a*]benzimidazole (**10b**) was obtained in 6% yield as white leaflets (EtOH): mp 202–203°; ir (KBr) 1740, 1710 ($COOCH_3$), 1655 cm^{-1} (CO); uv λ_{max}^{EtOH} 243 nm (log ϵ 4.72), 312 (4.09), 325 (3.99); nmr δ 1.31 (triplet, NCH_2CH_3), 3.88, 4.05 [singlet, $(COOCH_3)_2$], 4.36 (quartet, NCH_2CH_3), 7.36 (singlet, 3-H), 7.50 (multiplet, aromatic protons), 8.12 (doublet, 6-H); mass spectrum *m/e* 328 (M^+). *Anal.* Calcd for $C_{17}H_{16}N_2O_5$: C, H, N.

4-Ethyl-1,2,3-tris(methoxycarbonyl)-4*H*-pyrrolo[1,2-*a*]benzimidazole (**9b**) was obtained as white prisms (2% yield): mp 134–135° (EtOH); ir (KBr) 1740, 1710, 1690 cm^{-1} ($COOCH_3$); uv λ_{max}^{EtOH} 215 nm (log ϵ 4.43), 247 (4.48), 292 (4.38), 331 (4.31); nmr δ 1.43 (triplet, NCH_2CH_3), 3.90, 3.95, 4.02 [singlet, $(COOCH_3)_3$], 4.76 (quartet, NCH_2CH_3), 7.33 (multiplet, aromatic protons), 8.40 (doublet, 8-H); mass spectrum *m/e* 358 (M^+). *Anal.* Calcd for $C_{18}H_{18}N_2O_6$: C, H, N.

Registry No.—**5a**, 34910-61-7; **5b**, 34910-62-8; **5c**, 34910-63-9; **5d**, 34910-64-0; **5e**, 34910-65-1; **5f**, 34910-66-2; **6a**, 34910-67-3; **6b**, 34934-78-6; **6c**, 34910-68-4; **6d**, 34910-69-5; **6e**, 34910-70-8; **6f**, 34910-71-9; **7**, 34910-72-0; **8a**, 34910-73-1; **8b**, 34910-74-2; **8d**, 34910-75-3; **8e**, 34910-76-4; **9a**, 14882-70-3; **9b**, 34910-78-6; **10a**, 34910-79-7; **10b**, 34915-98-5.

The Cycloaddition of Vinyl Azides to Ketenes[1]

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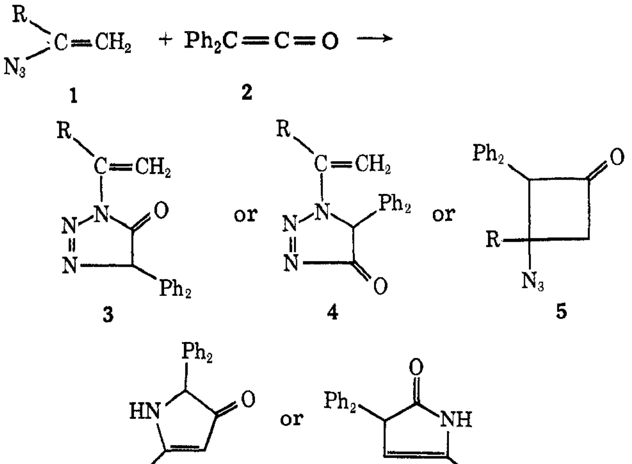
Vinyl azides undergo slow cycloaddition with diphenylketene (**2**) leading to five-membered ring enamino ketones **6** with loss of N_2. The reaction appears to involve nucleophilic attack of the β carbon from the vinyl azide upon the ketene. A substantial improvement in yield of **6** is achieved by generating **2** *in situ* from a diazo ketone in solution. Treatment of the enamino ketones with phosphorus pentachloride or chlorine leads to α chlorination. In the case of 2-azido-1-hexene, cycloaddition with **2** proceeds with formation of cyclobutanones.

The azide group represents a versatile function which can act as a nucleophile, electrophile, or 1,3 dipole.[2] An adjacent C=C, as in vinyl azides, accentuates or modifies the chemical behavior of this functional group.[3] Thus, vinyl azides exhibit a markedly greater reactivity than alkyl azides in cycloadditions with acetylenes.[4] Although the reaction of ketenes with olefins and imines has received a great deal of attention,[5] there appears to be no report of their interaction with azides.[6a] If one considers the cycloaddition of vinyl azides **1** to ketenes (*e.g.*, **2**) leading primarily to 1:1 adducts, one can envisage products of type **3**–**7** that might arise *via* a concerted or stepwise pathway.

Furthermore, in protonation and bromination of vinyl azides **1** it is difficult to distinguish whether the electrophile attacks one of the nitrogens or the β carbon of the unsaturated azide.[3] A product analysis of the reaction of **1** with ketenes offers the opportunity to establish any regiochemical preference in the cycloaddition (for instance preferential formation of **3** *vs.* **4** or **6** *vs.* **7**).



Results and Discussion

α-Azidostyrene (**1**, R = Ph) undergoes a slow reaction with diphenylketene (**2**) in ether at room temperature producing a 1:1 adduct with loss of N_2. Although the yield of this adduct was only 7% after a 3-day reaction, no other product was detected and a considerable amount of starting vinyl azide was present, together

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[1] Cycloadditions. VIII. For previous paper in the series see ref 7.

[2] G. L'abbé, *Chem. Rev.*, **69**, 345 (1969).

[3] See, for instance, (a) A. Hassner, E. S. Ferdinandi, and R. J. Isbister, *J. Amer. Chem. Soc.*, **92**, 1672 (1970); (b) A. Hassner and A. B. Levy, *ibid.*, **93**, 5469 (1971).

[4] G. L'abbé, J. E. Galle, and A. Hassner, *Tetrahedron Lett.*, 303 (1970); G. L'abbé and A. Hassner, *Bull. Soc. Chim. Belg.*, **80**, 209 (1971).

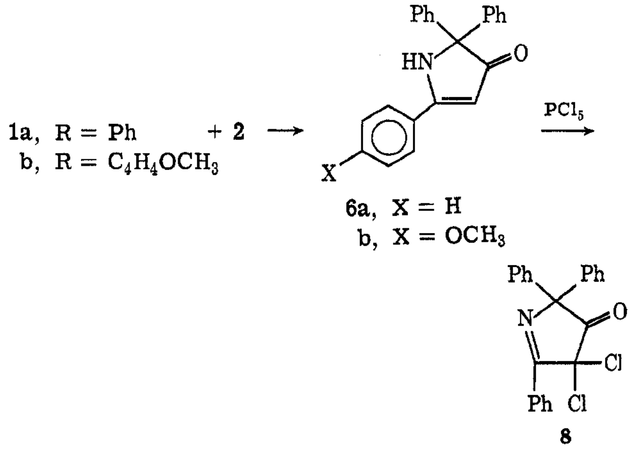
[5] See, for instance, (a) W. T. Brady, *Synthesis*, 415 (1971); R. Huisgen, B. A. Davis, and M. Morikan, *Angew. Chem., Int. Ed. Engl.*, **7**, 826 (1968); (b) J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, Jr., *J. Org. Chem.*, **36**, 2211 (1971).

[6] (a) Only the intramolecular decomposition of azido ketenes has been described: A. Hassner, R. J. Isbister, R. B. Greenwald, J. T. Klug, and E. C. Taylor, *Tetrahedron*, **25**, 1637 (1969). (b) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).

with some polymeric material. Heating of the reaction mixture did not lead to higher yields of cycloadduct but instead caused polymerization and conversion of the vinyl azide into 2-phenylazirine,[6b] which in turn reacted[7] with diphenylketene to produce a bicyclic aziridine (1:2 adduct). To avoid the presence of large amounts of diphenylketene (**2**), which undergoes polymerization, we generated **2** *in situ* by refluxing a solution of **1a** and α-diazo-α-phenylacetophenone in benzene. In this manner the yield of the adduct increased to 50%.

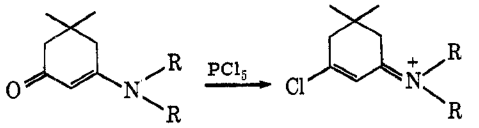
Structure **6a** was established for the 1:1 adduct, mp 300°, on the basis of the following spectral data and chemical reactions. The ir spectrum of **6a** contains NH absorptions at 3200 and 1580 cm^{-1} which shift on deuterium exchange, as well as a carbonyl band at 1620 cm^{-1}, typical of enamino ketones (vinylogous amides).[8] The compound exhibits a vinyl proton at τ 4.45 and NH (exchangeable with D_2O) at 0.77 in the nmr (in DMSO-d_6). The uv spectrum indicates extensive conjugation at 248 nm (ϵ 22,500) and 351 (8000). The molecular ion appears at m/e 311 in the mass spectrum with the base peak at m/e 282 (M^+ − HCO). The possibility that the adduct possessed structure **7** was dismissed on the basis of comparison with an authentic sample of **7**.[9]

As a vinylogous amide, **6a** did not form an oxime derivative on refluxing with $NH_2OH \cdot HCl$–pyridine. It was also unreactive toward $LiAlH_4$, apparently because of the resistance of the primarily formed anion to further attack by hydride. Whereas vinylogous amides of type **9** were reported to give **9a** on heating with PCl_5,[10] reaction of **6a** with PCl_5 in refluxing benzene led to the dichloro derivative **8** in 57% yield. In this reaction, chlorination of the enamine carbon is favored over that of the carbonyl carbon[10] by two factors: (a) the steric effect imposed by the phenyl groups; (b) a possible higher nucleophilicity of the enamine carbon.



6a, X = H
b, X = OCH_3

8

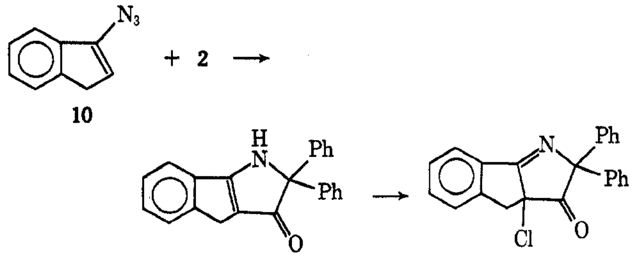


9 **9a**

The same product **8** was obtained in quantitative yield on chlorination of **6a** in benzene. The ir spectrum of **8** shows carbonyl absorption, typical of a dichlorocyclopentanone, at 1780 cm^{-1} and conjugated C=N at 1605 cm^{-1}. NH absorptions were absent. The uv maximum at 254 nm (ϵ 14,500) is similar to that of benzalmethylamine at 247 nm (ϵ 15,900).

p-Methoxy-α-azidostyrene (**1b**) reacted with diphenylketene (**2**) to produce an analogous adduct **6b**. The cycloaddition proceeded faster than with **1a**, indicating a stabilizing effect in the transition state by virtue of the contribution of the *p*-methoxy group to the nucleophilicity of the β carbon in **1** (see **1** + **2** → **13** below). The spectral and chemical properties of enamino ketone **6b** were similar to those of **6a**.

An analogous cycloadduct **11** was formed from 1-azidoindene (**10**) and **2**. This vinyl azide was chosen because of its known reluctance to form an azirine on heating;[7] hence, heating of the reaction mixture is expected to lead to an improved yield of **11**. Indeed the yield increased from 7% in ether and 11% in DMF at 25° to 35% in refluxing THF. The spectral properties of **11** [NH at 3250 and 1580 cm^{-1}, C=O at 1625 cm^{-1}, CH_2 singlet at τ 6.56, NH at τ 0.65, uv absorption at 248, 345, and 362 nm (ϵ 16,400, 5700, and 5800, respectively)] are consistent with its structure. Reaction of **11** with PCl_5 permits only monochlorination and led to 3-chloro-5,5-diphenylindeno[1,2-*b*]-1-pyrolin-4-one (**12**) in 34% yield.

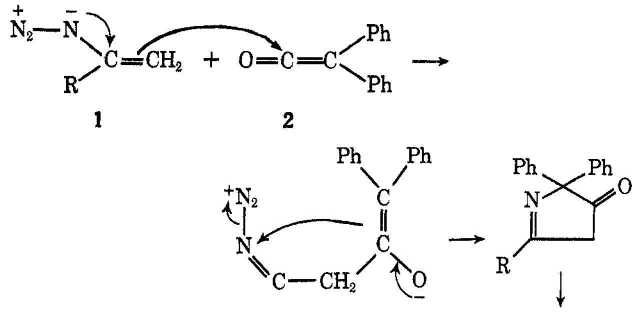


10

11 **12**

1-Azidoindene (**10**) was the only β-substituted vinyl azide that was found to react with diphenylketene. 1-Azido-*cis*-1-phenylpropene, α-azido-*trans*-stilbene, and 1-azido-2-*tert*-butylethene gave no adducts with **2**. In one case an azirine–ketene adduct[7] was isolated. These data indicate a steric effect at the β carbon of the vinyl azide during the cycloaddition and are reminiscent of the decrease in rate of dipolar cycloadditions observed upon increased hindrance in the olefin.[11]

The presented results can be rationalized by an ionic mechanism (**1** → **13** → **6**) whereby a nucleophilic attack



1 **2**

13 **6**

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(7) A. Hassner, A. S. Miller and M. J. Haddadin, *Tetrahedron Lett.*, 1353 (1972).

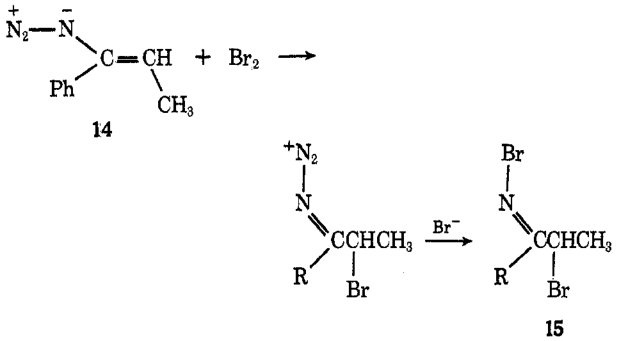
(8) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *J. Amer. Chem. Soc.*, **71**, 3337 (1949); A. I. Meyers, A. H. Reine, and R. Gault, *J. Org. Chem.*, **34**, 698 (1969).

(9) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 662 (1890).

(10) G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 794 (1964).

(11) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).

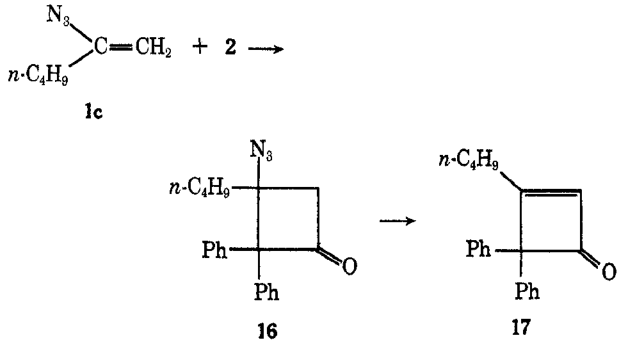
by the β carbon of **1** upon the C=O of the ketene is facilitated by electron donation from nitrogen. Such a pathway is analogous to that of the reaction of enamines with ketene.[12] The process resembles the mechanism observed in bromination of vinyl azides (**14** → **15**),[3b] where nucleophilic attack through carbon



14 **15**

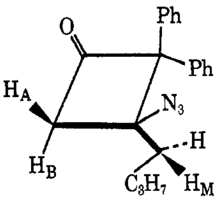
was postulated. In the reaction with ketene **2**, isolation of products **6** rather than of the regioisomeric **7** indicates that nucleophilic attack by C is preferred to attack by N. In the cases reported here ring closure with loss of N_2, as shown in **13**, is followed by tautomerization to the enamino ketone **6**.

The cycloaddition of diphenylketene (**2**) with vinyl azide **1c**, which contains an aliphatic substituent at the azido carbon, proceeded in a different manner. The major product (30% by nmr) was the azidocyclobutanone **16**. Cyclobutenone **17** and a 3:1 adduct

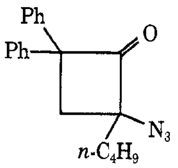


1c **16** **17**

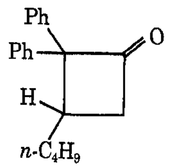
(not further characterized) were also formed.[13] The structure of **16** was apparent from its spectral and chemical properties. The ir absorption at 1780 cm^{-1} is characteristic of cyclobutanones and the bands at 2110 and 1200 cm^{-1} of an azide group. The methylene hydrogens in the cyclobutanone ring appear in the nmr as two doublets at τ 7.03 and 6.68 (J = 17.7 Hz), with the latter further split into a quartet (J = 0.9 Hz). This is attributable to long-range coupling (W effect) between H_M of the n-butyl group and the trans ring proton H_A (deshielded by the cis azide function) in the sterically preferred conformation **16a**. The reaction product is not likely to possess the regioisomeric structure **18**, since such a product would not be expected to eliminate HN_3 with ease. Moreover, structure **16** is consistent with the above behavior of vinyl azides **1** where the β carbon is the nucleophilic site in the reactant.[14]



16a



18



19

Cyclobutenone **17** was shown to be a secondary product in the reaction, as evidenced by its formation from **16** on stirring with Merck alumina for 1.5 days. **17** shows absorption at 1750 (C=O) and 1580 cm^{-1} (C=C). In the nmr the vinyl proton absorption at τ 3.75 appears as a multiplet due to long-range coupling with the allylic hydrogens in the side chain. The latter absorb as a broad triplet at τ 7.35. Catalytic hydrogenation of **17** proceeds rapidly to furnish 3-n-butyl-2,2-diphenylcyclobutanone (**19**) (ir 1775 cm^{-1}) in 73% yield.

If one considers intermediate **13** as the first step in the reaction, the formation of a five-membered ring *vs.* a four-membered ring adduct from **1a** and **1b** can be rationalized on the basis of an inductive effect by the aryl group which promotes nucleophilic attack at N. It is unlikely that azidocyclobutanones are precursors of **6** and **11** because pyrolysis of **16** does not lead to any detectable amounts of **6** (R = n-C_4H_9). Whether the formation of cyclobutanone **16** proceeds by a concerted ${}_{\pi}2_s + {}_{\pi}2_a$ cycloaddition or by a stepwise process remains to be established.

Experimental Section[15]

2,5,5-Triphenyl-2-pyrrolin-4-one (6a).—To 0.55 g (3.8 mmol) of α-azidostyrene (**1a**) dissolved in 40 ml of anhydrous diethyl ether was added 0.80 g (4.1 mmol) of diphenylketene (**2**).[16] The reaction mixture was stirred for 3 days and the solid (0.13 g, 12%) was filtered, washed with cold ether, and recrystallized from benzene. The yield of pure **6a** was 0.08 g (7%): mp 300°; ir (KBr) 3200 (after exchange with D_2O, 2340), 1620, 1599, 1580, 1540 cm^{-1}; nmr (DMSO-d_6, 60°, HA-100) τ 4.45 (s, 1, C=CH), 1.85–3.19 (m, 15, phenyl hydrogens), −0.77 (s, broad, NH, exchangeable with D_2O); uv max (p-dioxane) 333 nm (ϵ 5900), 247 (17,700); uv (95% C_2H_5OH) 351 nm (ϵ 8000), 248 (22,500); mass spectrum (70 eV) m/e (rel intensity) 311 (54, M^+), 282 (100), 206 (26), 204 (30), 180 (22), 178 (30), 165 (26).

Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 85.06; H, 5.43; N, 4.34.

An nmr spectrum of the remaining reaction mixture shows the presence of a considerable amount of vinyl azide but no cyclobutanone.

In an alternate procedure a solution of 1.4 g of **1a** in 20 ml of benzene containing 2.2 g of α-diazo-α-phenylacetophenone[17] was heated on a steam bath for 1 hr. **6a** precipitated during the reaction. The slurry was cooled and **6a** was filtered off (1.6 g, 51% yield).

Enamino ketone **6a** was recovered unchanged (86–100%) upon exposure to $LiAlH_4$ in THF for 24 hr or upon heating with $NH_2OH \cdot HCl$ and pyridine for 19 hr.

3,3-Dichloro-2,5,5-triphenyl-1-pyrrolin-4-one (8).—To 0.5 g (1.6 mmol) of **6a** in 50 ml of dry benzene was added 1 g (4.8

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[12] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

[13] 3:1 adducts from the reaction of ketene with enamines have been reported (ref 12).

[14] The possibility that the reaction product of **1c** + **2** might be **18** was raised by one of the referees.

[15] Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrometer and nmr spectra on a Varian A-60A spectrometer. Mass spectra were taken on a Varian M.A.T. CH-5. All solvents were either reagent grade or distilled before use. All vinyl azides and azirines were prepared by the method of A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968), and ref 6.

[16] L. I. Smith and H. H. Hoehn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 356.

[17] C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 496.

mmol) of PCl_5. The solution was refluxed for 3 hr. After the solution had cooled, 5 ml of H_2O was added with stirring. The organic layer was separated and the solvent was evaporated. The residue (0.47 g, composed of 100% **8** as determined by nmr) was recrystallized from CH_3CN–H_2O (50:50) to give 0.38 g (57%) of **8**: mp 171–172°; ir (KBr) 1780, 1605, 1500 cm^{-1}; nmr ($DCCl_3$) τ 2.35–3.90 (m, 13, phenyl hydrogens), 1.45–1.90 (m, 2,2-phenyl ortho hydrogens); uv max (95% C_2H_2OH) 254 nm (ϵ 14,500); mass spectrum (70 eV) *m/e* (rel intensity) 383:381: 379 (M^+) in a ratio of 1:5:7 (very weak), 317 (59), 165 (100).

Anal. Calcd for $C_{22}H_{15}Cl_2NO$: C, 69.48; H, 3.98. Found: C, 69.31; H, 4.13.

The same product **8** was obtained in quantitative yield by bubbling excess Cl_2 into a slurry of **6a** in benzene and subsequent evaporation of the benzene.

***p*-Methoxy-α-azidostyrene** (**1b**).—The synthesis of **1b** from *p*-methoxystyrene and iodine azide was modeled after that described for styrene.[13] DBN was used as the base in the elimination of HI from the iodine azide adduct. The vinyl azide **1b** was purified by dissolving the solid in a minimum amount of pentane and passing the solution through a disposable pipette filled with neutral alumina: mp 31–32°; ir (CCl_4) 2830, 2140, 2100, 1610 cm^{-1}; nmr (CCl_4) τ 2.65 (d, 2, J = 9 Hz, aromatic hydrogens), 3.32 (d, 2, J = 9 Hz, aromatic hydrogens), 4.33 (d, 1, J = 2 Hz, olefinic hydrogen), 5.30 (d, 1, J = 2 Hz, olefinic hydrogen), 6.38 (s, 3, OCH_3).

2-(*p*-Methoxyphenyl)-5,5-diphenyl-2-pyrrolin-4-one (**6b**).—From the reaction of 0.5 g (2.8 mmol) of *p*-methoxy-α-azidostyrene (**1b**) and 0.6 g (3.1 mmol) of diphenylketene (**2**) for 3 days as described for **6a**, there was obtained 0.3 g of a very insoluble compound. Purification was accomplished by absorbing 0.1 g of the solid on 2 g of silica gel and eluting the absorbed compound over 20 g of silica gel with benzene–ether (80:20). In this manner 0.66 g (16%) of **6b** was obtained: mp >300°; ir (KBr) 3200, 1625, 1600, 1580, 1560 cm^{-1}; nmr (DMSO-d_6, 100°, HA-100) τ 1.02 (s, 1, NH, exchangeable with D_2O), 2.02–3.34 (m, 14, phenyl hydrogens), 4.61 (s, 1, C=CH); uv max (95% C_2H_5OH) 282 nm (ϵ 20,000), 352 (12,000); mass spectrum (70 eV) *m/e* (rel intensity) 341 (82, M^+), 312 (100), 208 (26), 132 (26).

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61. Found: C, 80.67; H, 5.58.

An nmr spectrum of the remaining reaction mixture shows the presence of 40% starting vinyl azide.

When the reaction was carried out by heating 0.85 g of **1b** with 1.1 g of α-diazo-α-phenylacetophenone in benzene at reflux for 15 min, **6b**, which precipitated during heating, was obtained in 45% yield (0.8 g).

5,5-Diphenylindeno[1.2-*b*]-2-pyrrolin-4-one (**11**).—From 8.1 g (52 mmol) of 1-azidoindene (**10**) in 100 ml of diethyl ether and 10 g (56 mmol) of diphenylketene (**2**) at 25° for 3 days there was obtained a powdery yellow solid. Recrystallization from benzene furnished 0.6 g of **11**: mp >300°; ir (KBr) 3260, 1625, 1605, 1540 cm^{-1}; nmr (DMSO-d_6, 100°, HA-100) τ 0.65 (s, 1, NH, exchangeable with D_2O), 2.14 (d, 1, hydrogen on indene), 2.48–2.18 (m, 13, phenyl hydrogens), 6.56 (s, 2, $-CH_2-$); uv max (dimethylformamide) 364 nm (ϵ 9100), 299 (3800), 285 (3500); uv (*p*-dioxane) 362 nm (ϵ 5800), 299 (4000), 289 (3900); mass spectrum (70 eV) *m/e* (rel intensity) 323 (56, M^+), 295 (32), 294 (100), 178 (32), 105 (50).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30. Found: C, 85.25; H, 5.31.

An nmr spectrum of the remaining reaction mixture shows mainly the presence of vinyl azide **10**.

When the reaction was carried out in DMF solution a tarry material coagulated on the side of the flask. It was dissolved in 50 ml of hot DMF, and the solution was filtered, cooled, and diluted with 50 ml of ether to precipitate 0.5 g (11%) of **11**.

From 10 g (64 mmol) of the vinyl azide **10** and 12.5 g (65 mmol) of the ketene **2** in 100 ml of THF under reflux for 3 days there was obtained 7.2 g (35%) of **11**.

3-Chloro-5,5-diphenylindeno[1,2-*b*]-1-pyrrolin-4-one (**12**).—A solution of 0.62 g (1.9 mmol) of **11** and 1.2 g (5.7 mmol) of PCl_5 in 50 ml of benzene was refluxed for 6 hr. Work-up as for **8** gave 0.57 g of crude **12**. Crystallization from CH_3CN–H_2O furnished 0.83 g (34%) of **12**: mp 128–129°; ir (KBr) 1770, 1640, 1500 cm^{-1}; nmr ($DCCl_3$) τ 6.65 (s, broad, 2, $-CH_2-$), 2.00–2.83 (m, 14, phenyl hydrogens); uv max (95% C_2H_5OH) 251 nm (ϵ 14,100).

Anal. Calcd for $C_{23}H_{16}ClNO$: C, 77.19; H, 4.51. Found: C, 76.98; H, 4.37.

3-Azido-2,2-diphenyl-3-*n*-butylcyclobutanone (**16**).—To 0.5 g (4 mmol) of 2-azido-1-hexene (**1c**) in 30 ml of anhydrous ether was added 1 g (5.1 mmol) of diphenylketene (**2**). The reaction mixture was stirred for 3 days. The precipitate, representing a 3:1 adduct, was filtered and weighed 0.06 g (4%), recrystallized from 95% C_2H_5OH: mp 218–218.5°; ir (KBr) 3260, 1740, 1640, 1130 cm^{-1}; nmr ($DCCl_3$) τ 2.73–3.12 (m, 30, phenyl hydrogens), 4.13 (broad, s, 1), 5.04 (s, 1), 7.50–7.90 (broad, s, 2), 8.67–9.50 (m, 9, aliphatic hydrogens); mass spectrum (70 eV) *m/e* (rel intensity) 681 (very weak), 439 (45), 318 (24), 212 (19), 167 (100), 166 (33), 165 (84).

The solvent was evaporated from the filtrate, yielding an oil (1.35 g). Chromatography on 50 g of silica gel with Skellysolve B as eluent afforded 0.27 g (21%) of **16** as an oil: ir (CCl_4) 2110, 1775, 1490, 1450, 1260 cm^{-1}; nmr (CCl_4) τ 2.32–3.03 (m, 10, phenyl hydrogens), 6.68 (d, 1, J = 17 Hz, OCCH trans to *n*-butyl), 7.03 (d, 1, J = 17 Hz, O=CCH cis to *n*-butyl), 7.91–9.50 (m, 9, $-C_4H_9$).

Anal. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63. Found: C, 75.02; H, 6.78.

An nmr spectrum of the crude reaction mixture (before chromatography) showed it to consist of 30% cyclobutanone **16** and 70% vinyl azide **1c**.

When the reaction was allowed to proceed for a week, 2% of **17** was also found among the products.

3-*n*-Butyl-4,4-diphenyl-2-cyclobutenone (**17**).—Crude azido ketone **16** (2.89 g) was dissolved in 100 ml of ether and added to Merck alumina, and the mixture was stirred for 1.5 days. The ether was decanted and the alumina was washed several times with small portions of ether. The ether washes were combined and the ether was evaporated. The oil (1.2 g) was crystallized from 2 ml of ethyl acetate–pentane (40:60). The white needles of **17**, weighing 0.3 g (25%), were filtered and dried: mp 73–75°; ir (CCl_4) 1750, 1580, 1490, 1440 cm^{-1}; nmr ($DCCl_3$) τ 2.70 (s 10, phenyl hydrogens), 3.75 (t, 1, C=CHC=O), 7.45 (t, 2, $C_3H_7CH_2C{=}C$), 8.08–9.30 (m, 7, C_3H_7); uv (*p*-dioxane) shoulders on end absorption at 345 nm (ϵ 5800), 362 (5800).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.79; H, 7.33.

3-*n*-Butyl-2,2-diphenylcyclobutanone (**19**).—To 0.026 g (0.09 mmol) of the cyclobutanone **17** was added 0.053 g of Pd/C (5%) and 20 ml of thiophene-free benzene. After the solution was flushed with nitrogen, hydrogen was bubbled through for 25 min at a rate of approximately 0.1 cc/sec. Nitrogen was again bubbled through the solution and the catalyst was filtered. The product was purified by chromatography on a 2-mm silica gel plate using benzene–Skellysolve B (50:50) as eluent, yielding 0.019 g (73%) of **19** recrystallized from pentane: mp 46–49°; ir (KBr) 1770 cm^{-1}; nmr ($DCCl_3$) τ 2.53–3.08 (m, 10, phenyl hydrogens), 6.47–7.36 (m, 3, $C_4CHCH_2C{=}O$), 8.29–9.45 (m, 7, n-C_3H_7).

Anal. Calcd for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.52; H, 8.05.

Registry No.—**1a**, 16717-64-9; **1b**, 34910-42-4; **1c**, 34910-43-5; **2**, 525-06-4; **6a**, 34910-44-6; **6b**, 34910-45-7; **8**, 34910-46-8; **10**, 16719-57-6; **11**, 34910-48-0; **12**, 34910-49-1; **16**, 34910-50-4; **17**, 34910-51-5; **19**, 24242-42-0; 2-azido-1-hexene–diphenyl ketene adduct (1:3), 34910-53-7.

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