Anal. Calcd for $C_{26}H_{14}NCl \cdot H_2O$: C, 70.3; H, 5.85; N, 5.1; Cl, 13.0. Found: C, 70.2; H, 5.65; N, 5.0; Cl, 13.0.

Oxidation.—The remaining benzylquinolinium chloride was oxidized to N-benzyl-N-formylanthranilic acid with potassium permanganate.[17]

Benzylquinolinium chloride (2.0 g) was dissolved in water (400 ml) and warmed to 30°. Potassium permanganate (4.12 g) dissolved in warm water (200 ml) was added over 2 hr with vigorous stirring. The reaction mixture was then made alkaline by the addition of a few pellets of solid potassium hydroxide and filtered. The filtrate was acidified with hydrochloric acid. The pale amber oil, that separated from the aqueous phase on acidification, solidified on standing. The solid was filtered and recrystallized ten times from ethyl alcohol to yield colorless granular crystals, mp 194°.

Anal. Calcd for $C_{15}H_{13}O_3N$: C, 70.6; H, 5.1; N, 5.5. Found: C, 70.5; H, 5.1; N, 5.5.

A sample of this purified product, dissolved in a dioxane-based scintillator, showed no detectable radioactivity.

Radioactivity Measurements.—Radioactivity measurements were made in a coincidence liquid scintillation counter.[18a] Nonquenching radioactive liquids were injected into weighed counting phials containing a suitable phosphor and sealed with rubber serum caps.[18b] Quenching liquids and solids (picrates) were burned in an oxygen flask combustion apparatus and the [^{14}C]carbon dioxide thus formed was dissolved in 2-phenylethylamine premixed with a liquid phosphor and injected into the flask.[18c] Counting efficiencies were measured with an "efficiency stick",[18d] and random samples were checked by "spiking" with a nonquenching standard.[18b]

Registry No.—1,2-Dihydroquinaldine, 1125-81-1; 1,2-dihydroquinaldine picrate, 15619-45-1; 1,2-dihydro-1,4-dimethylquinoline, 15619-46-2; 1,2-dihydro-2,4-dimethylquinoline picrate, 15619-47-3; benzylquinolinium chloride (VII), 15619-48-4; 1-benzyl-N-formylanthranilic acid (VIII), 15656-73-2; [^{14}C] bromo-form, 7825-2; [^{14}C]methylene bromide, 15619-50-6.

Acknowledgments.—Thanks are extended to Dr. W. A. Waters, F. R. S., Dr. K. W. Bentley, and Dr. G. T. Rogers for their advice and to D. G. Humphreys for technical assistance.

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[17] A. Claus and F. Glyckherr, *Chem. Ber.*, **16**, 1283 (1883).

[18] H. E. Dobbs: (a) U. K. Atomic Energy Authority Memorandum, AERE-M1075 (1962); (b) U. K. Atomic Energy Authority Memorandum, AERE-M1574 (1965); (c) *Anal. Chem.*, **35**, 783 (1963), and **36**, 687 (1963); (d) *Nature*, **200**, 1283 (1963).

Aziridines. XVIII. Reactions of a 1,3-Diazabicyclo[3.1.0]hex-3-ene with Alkenes, Alkynes, and Diethyl Azodicarboxylate

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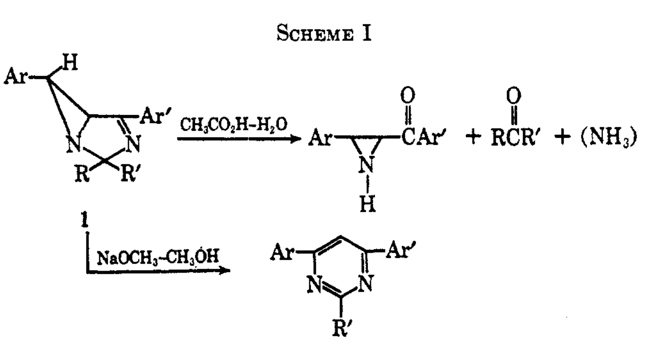
Adducts of 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene with diethylacetylene dicarboxylate, diethyl fumarate, *cis*- or *trans*-dibenzoylethene, diethyl azodicarboxylate, and N-phenylmaleimide are formed in refluxing *p*-xylene. The reaction proceeds by carbon–carbon bond scission of the aziridine ring of the 1,3-diazabicyclo[3.1.0]hex-3-ene.

The synthesis of the previously unknown class of compounds, the 1,3-diazabicyclo[3.1.0]hex-3-enes (1), has been described recently.[1] Some of these compounds are converted in moist acetic acid into 2-aryl-3-aroylaziridines and ketones. Other 1,3-diazabicyclo-[3.1.0]hex-3-enes (where R = H) in methanol containing sodium methoxide rearrange and subsequently air oxidize into pyrimidines (Scheme I).

SCHEME I



We now have observed that in refluxing *p*-xylene 1,3-diazabicyclo[3.1.0]hex-3-enes form adducts with various alkenes, alkynes, and diethyl azodicarboxylate. The adducts are novel bicyclic or tricyclic systems and are formed by carbon–carbon cleavage of the aziridine ring. Recent work has demonstrated that carbon–carbon scission of the aziridine ring occurs when 1,2,3-triarylaziridines,[2] 2-aroylaziridines,[3] 2,3-diaroylaziridines,[4] and 2,3-dicarbethoxyaziridines[5] are heated in inert solvents with alkenes and alkynes.

Results

Refluxing a *p*-xylene solution of 2,2-dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (2) and diethylacetylene dicarboxylate formed diethyl 3,3-dimethyl-5-(*p*-nitrophenyl)-1-phenyl-3H-pyrrolo-[1,2-*c*]imidazole-6,7-dicarboxylate (3) (Scheme II). The structure of 3 was confirmed by acid hydrolysis to 2-benzoyl-3,4-dicarbethoxy 5-*p*-nitrophenylpyrrole (4) and presumably acetone. The hydrolysis of the 3-imidazoline moiety of 3 is analogous to the acid hydrolysis of 3-imidazolines to form α-amino ketones, ketones, and ammonium chloride[6] and of 1,3-diazabicyclo[3.1.0]-hex-3-enes to form 2-aryl-3-aroylaziridines and ketones.[1] The structure of 4 was assigned by means of an independent synthesis involving the addition of *trans*-2-*p*-nitrophenyl-3-benzoylaziridine (5) to di-

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[1] H. W. Heine, R. H. Weese, R. A. Cooper, and A. J. Durbetaki, *J. Org. Chem.*, **32**, 2708 (1967).

[2] H. W. Heine and R. E. Peavy, *Tetrahedron Lett.*, 3123 (1965); H. W. Heine, R. E. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966).

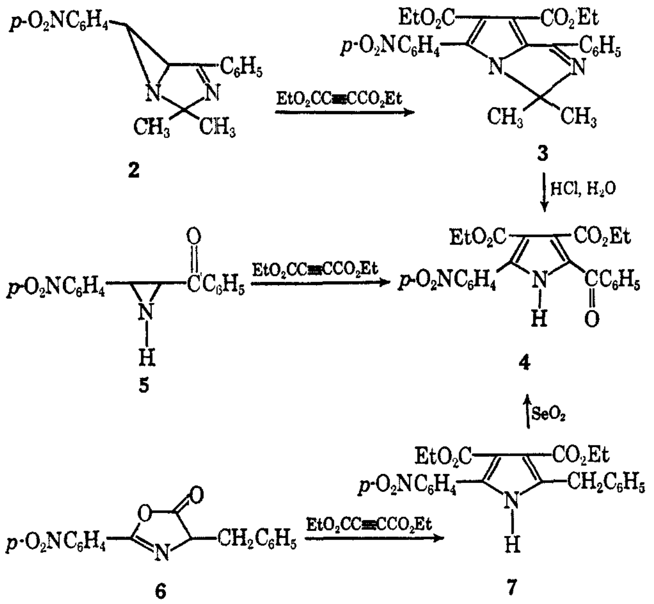
[3] A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 4363 (1965); A. Padwa and L. Hamilton, *J. Heterocyclic Chem.*, **4**, 118 (1967).

[4] R. Huisgen, W. Scheer, G. Szemies, and H. Huber, *Tetrahedron Lett.*, 397 (1966).

[5] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

[6] G. Kirchner, *Ann.*, **625**, 98 (1959).

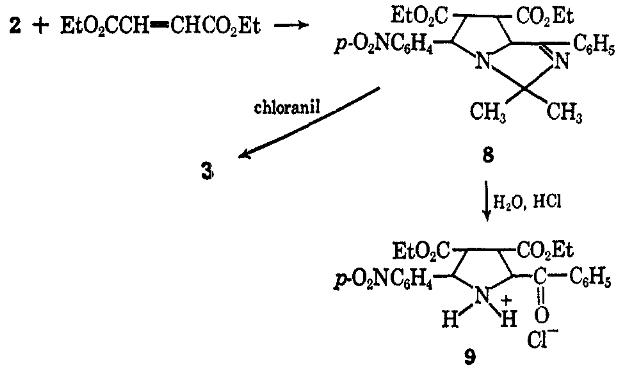
SCHEME II



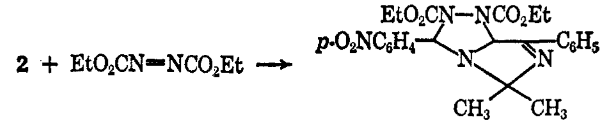
ethylacetylene dicarboxylate. Padwa and Hamilton had previously demonstrated that *trans*-2-phenyl-3-benzoylaziridine adds to dimethylacetylene dicarboxylate by carbon–carbon scission of the aziridine ring to yield 2-benzyl-3,4-dicarbomethoxy-5-phenylpyrrole.[3] Compound **4** was also prepared by a two-step process involving first the heating of 2-*p*-nitrophenyl-4-benzyl-5-oxazolone (**6**) with diethylacetylene dicarboxylate which gave 2-benzyl-3,4-dicarbomethoxy-5-*p*-nitrophenylpyrrole (**7**). Compound **7** was subsequently oxidized by selenium dioxide to **4**. A similar sequence has been employed to prepare 2-benzoyl-3,4-dicarbomethoxy-5-phenylpyrrole.[3]

Compound **2** readily reacted with diethyl fumarate to form the adduct **8**. The structure of **8** was confirmed by the chloranil oxidation of **8** to **3**. Acid hydrolysis of **8** gave the pyrrolidine hydrochloride **9** (Scheme III).

SCHEME III

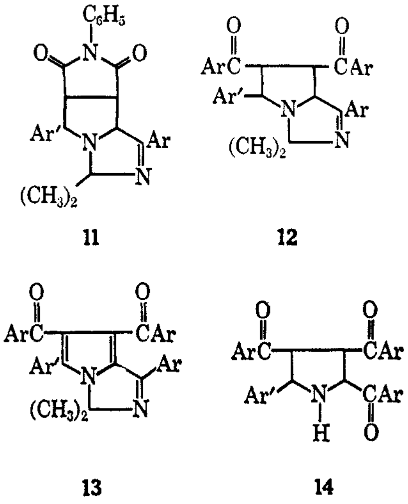


Refluxing of **2** with diethyl azodicarboxylate in *p*-xylene gave diethyl 5,7a-dihydro-5,5-dimethyl-3-(*p*-nitrophenyl)-7-phenyl-1H-imidazo[5,1-*c*]-*s*-triazole-1,2-(3H)-dicarboxylate (**10**). The structure of **10** was assigned on the basis of elemental analyses and nmr spectroscopy. The nmr spectrum showed the two methyl groups at C-5 as two singlets at 1.57 and 1.69 ppm, the two methine protons as a singlet at 6.51 ppm, and the two ethyl groups as two quartets centered at 4.0 ppm and two triplets clustered at 0.93 ppm downfield from tetramethylsilane as well as a complex pattern of bands from 7.2 to 8.3 ppm characteristic of aromatic protons. If the adduct **10** had been formed by carbon–nitrogen bond cleavage of the aziridine ring, the methine protons would be on adjacent carbon atoms and two doublets should be observed in the nmr spectrum.



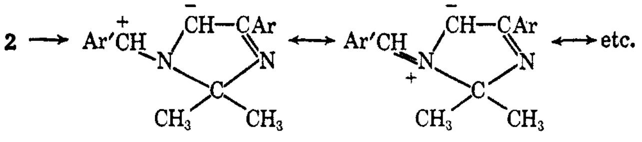
10

Compound **2** with N-phenylmaleimide in refluxing *p*-xylene gave 5,6,7,7a-tetrahydro-3,3-dimethyl-5-(*p*-nitrophenyl)-N,1-diphenyl-3H-pyrrolo[1,2-*c*]imidazole-6,7-dicarboximide (**11**). Refluxing equimolar quantities of **2** with *cis*- or *trans*-dibenzoylethene gave the identical addition product **12**. Control runs with *cis*- and *trans*-dibenzoylethenes in refluxing *p*-xylene showed that the interconversion of these alkenes does not occur. Compound **12** was oxidized by chloranil to the corresponding pyrrolo derivative **13**. Hydrolysis of compound **12** formed the pyrrolidine **14**. An independent synthesis of **14** was accomplished by the addition of *trans*-2-*p*-nitrophenyl-3-benzoylaziridine to *trans*-1,2-dibenzoylethene.



Ar = C_6H_5; Ar′ = $p\text{-}O_2NC_6H_4$

A likely mechanism for these additions is the conversion of the 1,3-diazabicyclo[3.1.0]hex-3-ene into a 1,3 dipole (**15**) which subsequently reacts with the unsaturated substrate.



15

The fact that **2** with *cis*- or *trans*-dibenzoylethene gave the same adduct **12** may be the result of a two-step nonstereoselective addition by the 1,3 dipole **15** to the ethenes. However, most 1,3-dipolar additions are known to be concerted and thus stereospecific.[7] More likely, the formation of the same stereoisomeric

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(7) R. Huisgen, *Angew. Chem.*, **2**, 633 (1963).

adduct **12** is the result of the epimerization of one of the initially formed adducts. The addition of diphenyl (nitrileimine) to dimethyl maleate has been shown to involve just such an epimerization.[7,8]

Experimental Section

2,2-Dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (2) was prepared either by the published procedure[1] or by the following shorter method. A suspension of 40.0 g of 2,3-dibromo-1-phenyl-3-(4-nitrophenyl)-1-propanone in 250 ml of absolute ethanol containing 10 ml of acetone was stirred and saturated with ammonia. When most of the dibromide had dissolved the reaction mixture was stored in a refrigerator overnight. The crude **2** was filtered and washed with a little 95% ethanol and then with water. Recrystallization from 95% ethanol gave 21.5 g (72%) of **2**.

Compound 3.—A mixture of 1.228 g of **2** and 680 mg of diethylacetylene dicarboxylate in 20 ml of *p*-xylene was refluxed for 1 hr. The solvent was evaporated and 4 ml of 95% ethanol was added to the oily residue. The crude **3** which formed on the addition of the ethanol weighed 945 mg (49%) and melted at 160–163°. Four recrystallizations from 95% ethanol gave **3** melting at 168–169.5°.

Anal. Calcd for $C_{26}H_{25}N_3O_6$: C, 65.68; H, 5.30; N, 8.84. Found: C, 66.01; H, 5.26; N, 9.15.

Compound 4. Method A.—A solution of 536 mg of *trans*-2-*p*-nitrophenyl-3-benzoylaziridine and 340 mg of diethylacetylene dicarboxylate in 5 ml of *p*-xylene was refluxed 1 hr. The solvent was evaporated and the oily residue heated with 5 ml of 95% ethanol. The crude **4** was filtered and weighed 125 mg (14%). Four recrystallizations from 95% ethanol gave **4** melting at 159–160°. A 22% yield of **4** was obtained if the oily residue was dissolved in a minimum amount of benzene and the benzene solution chromatographed on a 1.5 × 15 cm alumina column. The column was eluted with a 3% solution of ethyl acetate and 97% benzene.

Anal. Calcd for $C_{23}H_{20}N_2O_7$: C, 63.29; H, 4.62; N, 6.42. Found: C, 63.17; H, 4.56; N, 6.53.

Compound 4. Method B.—A solution of 200 mg of **3** in 10 ml of commercial absolute ethanol and 5 ml of concentrated hydrochloric acid was refluxed 1 hr. The solvent was evaporated and the residue recrystallized several times from 95% ethanol. The residue weighed 110 mg (60%) and melted at 159–160°.

Compound 4. Method C.—A mixture of 900 mg of **7** and 600 mg of selenium dioxide was sealed in a tube which was then heated in an oven at 200° for 75 min. The cooled reaction mixture was dissolved in a minimum quantity of benzene and the benzene solution was chromatographed on a column of alumina. The column was eluted with 3% ethyl acetate–97% benzene. Evaporation of the solvent from the collected fractions gave a heavy dark green oil. The green oil was heated in a minimum amount of hot 95% ethanol. On cooling the crystals of **4** which precipitated were collected (70 mg).

Compound 7.—A mixture of 1.5 g of 2-*p*-nitrophenyl-4-benzyl-2-oxazoline-5-one (**6**)[9] and 1.00 g of diethylacetylene dicarboxylate was sealed in a tube which was heated in an oven at 160° for 3 hr. The reaction mixture was cooled and dissolved in a minimum quantity of benzene. The benzene solution was chromatographed on a 1.5 × 15 cm alumina column. The eluate was 3% ethyl acetate–97% benzene. Evaporation of the eluent gave 700 mg (33%) of crude **7**. Recrystallization from 95% ethanol gave **7**, mp 166–167°.

Anal. Calcd for $C_{23}H_{22}N_2O_6$: C, 65.40; H, 5.25; N, 6.63. Found: C, 65.41; H, 5.04; N, 6.65.

Compound 8.—A mixture of 614 mg of **2** and 344 mg of diethyl fumarate in 20 ml of *p*-xylene was refluxed for 1 hr. The *p*-xylene was evaporated and 10 ml of 95% ethanol was added to the oily residue. The crude **8** was filtered and weighed 657 mg (68%) and melted at 165–167°. Four recrystallizations from 95% ethanol gave **8** melting at 165–167°.

Anal. Calcd for $C_{26}H_{29}N_3O_6$: C, 65.13; H, 6.09; N, 8.76. Found: C, 65.08; H, 6.33; N, 8.77.

Oxidation of 8 to 3.—A solution of 480 mg of **8** and 300 mg of chloranil in 10 ml of *p*-xylene was refluxed for 17 hr. The solvent was evaporated and the residue washed with ether. Recrystallization of the crude **3** with 95% ethanol gave 200 mg (42%) of **3**, mp 168–169°.

Hydrolysis of 8 to 9.—A solution of 1.3 g of **8** in 5 ml of concentrated hydrochloric acid and 5 ml of ethanol was refluxed for 15 min. Evaporation of the solvent and recrystallization of the residue from 95% ethanol gave **9**, mp 184–186°.

Anal. Calcd for $C_{23}H_{25}ClN_2O_7$: C, 57.91; H, 5.28; N, 5.87. Found: C, 57.95; H, 5.23; N, 5.85.

Compound 10.—A mixture of 920 mg of **2** and 600 mg of diethyl azodicarboxylate in 75 ml of decane was refluxed for 30 min. The solvent was evaporated and the crude **10** (1.10 g, 76%) was recrystallized once from 95% ethanol and four times from petroleum ether (bp 100–115°) to give **10** melting at 119–120°.

Anal. Calcd for $C_{24}H_{27}N_5O_6$: C, 59.86; H, 5.65; N, 14.54. Found: C, 60.26; H, 5.66; N, 14.83.

Compound 11.—A mixture of 614 mg of **2** and 346 mg of N-phenylmaleimide in 10 ml of *p*-xylene was refluxed for 1.5 hr. The *p*-xylene was evaporated and to the residual oil was added 20 ml of 95% ethanol. The crude **11** which precipitated was filtered and weighed 685 mg (71%); it melted at 218–219°. Four recrystallizations from ethanol gave **11** melting at 218–220°.

Anal. Calcd for $C_{28}H_{24}N_4O_4$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.20; H, 5.44; N, 11.78.

Compound 12. Method A.—A mixture of 614 mg of **2** and 472 mg of *trans*-dibenzoylethene in 10 ml of *p*-xylene was refluxed for 85 min. The solvent was evaporated and the solid residue recrystallized from 95% ethanol to give 728 mg (67%) of **12**, mp 200–202°.

Anal. Calcd for $C_{34}H_{29}N_3O_4$: C, 75.12; H, 5.37; N, 7.73. Found: C, 75.44; H, 5.59; N, 7.61.

Compound 12. Method B.—The identical procedure was employed as in method A above except 472 mg of *cis*-dibenzoylethene was employed in place of *trans*-dibenzoylethene. A 40% yield of **12** was obtained.

Oxidation of 12 into 13.—A solution of 543 mg of **12** and 600 mg of chloranil in 20 ml of *p*-xylene was refluxed for 17 hr. The solvent is evaporated and the residue washed with ether. The crude **13** weighed 520 mg and was recrystallized from 95% ethanol. The recrystallized **13** melted at 203–204°.

Anal. Calcd for $C_{34}H_{25}N_3O_4$: C, 75.66; H, 4.66; N, 7.78. Found: C, 75.60; H, 4.48; N, 7.63.

Compound 14. Method A.—To 5 ml of *p*-xylene was added 268 mg of *trans*-2-*p*-nitrophenyl-3-benzoylaziridine and 236 mg of *trans*-dibenzoylethene. This mixture was refluxed for 40 min and the solvent was then evaporated. The residue was slurried with a small quantity of ethanol and the crude **14** (322 mg, 65%) was filtered. Recrystallization from 95% ethanol gave **14** melting at 172–173°.

Anal. Calcd for $C_{31}H_{24}N_2O_5$: C, 73.79; H, 4.79; N, 5.55. Found: C, 73.65; H, 4.58; N, 5.71.

Compound 14. Method B.—A mixture of 310 mg of **12**, 10 ml of concentrated hydrochloric acid, and 10 ml of 95% ethanol was warmed for a few minutes on a hot plate. Not all of **12** dissolved. Prolonged heating is very detrimental to the isolation of **14**. The mixture was allowed to stand for 3 days during which time the color of the reaction mixture darkened considerably. The insoluble material was filtered. It presumably was the hydrochloride of **14**. Recrystallization of this material several times from 95% ethanol gave 114 mg of **14** that was identical in all respects with the **14** isolated in method A.

Registry No.—**3**, 15757-44-5; **4**, 15757-45-6; **7**, 15757-46-7; **8**, 15757-47-8; **9**, 15757-48-7; **10**, 15757-49-0; **11**, 15757-50-3; **12**, 15757-51-4; **13**, 15757-52-5; **14**, 15757-53-6; **2**, 15757-54-7.

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(8) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

(9) P. Karrer and C. Christoffel, *Helv. Chim. Acta*, **27**, 622 (1944).