dehyde in 10 ml of dry ether. After 2 hr the mixture was poured into 100 ml of 10% NH_4Cl solution. Extraction of the reaction product with chloroform and washing, drying, and evaporating of the solvent left 3.9 g (95%) of a solid: mp (benzene–petroleum ether) 68.5–69.5°; nmr ($CDCl_3$) δ 1.64–1.92 (m, 4, $-CH_2CH_2-$), 3.72–4.03 (m, 4, dioxolane protons); ir (KBr) 3300 cm^{-1} broad OH absorption.

4-Hydroxy-4-pyridylbutanal (as Hemiacetal 5b). A solution of 3.6 g (0.017 mol) of **4b** in 50 ml of 10% aqueous sulfuric acid was refluxed for 30 min. The mixture was cooled, made alkaline with 5 *N* NaOH, and extracted with chloroform. After drying and evaporation of the solvent the residual oil was chromatographed over SiO_2 ($CHCl_3$–2% CH_3OH as eluent) and afforded 2.3 g (8) of **5b**: mp ($CHCl_3$–(*i*-Pr)$_2O$) 117–118°; nmr ($CDCl_3$) δ 1.38–2.70 (m, 4, $-CH_2CH_2-$), 8.04 (ab, 4, pyridine protons); the ir spectrum (KBr) showed no C=O absorption, only broad OH band at 3300 cm^{-1}.

Dihydro-5-(4-pyridyl)-2(3*H*)-furanone (6b). To a solution of 0.33 g (0.002 mol) of **5b** in 20 ml of xylene was added 5.9 g of Ag_2CO_3–Celite (prepared according to the method of Fetizon; five times molar excess). The mixture was refluxed with stirring for 0.5 hr (on monitoring the reaction by tlc). After filtering the reaction mixture and stripping off the solvent, 0.16 g (48%) of **6** was obtained, as a solid: mp 56–57°; ir (KBr) strong C=O lactone absorption at 1760 cm^{-1}; nmr ($CDCl_3$) δ 1.93–3.18 (m, 4, $-CH_2CH_2-$), 5.57 (t, 1, CH), 8.00 (ab, 4, pyridine protons).

Registry No.—**2a**, 500-22-1; **2b**, 872-85-5; **2c**, 39269-79-9; **2d**, 39269-74-4; **2e**, 24134-12-1; **2f**, 10045-65-5; **2f** corresponding carbinol, 5376-10-3; **2g**, 13750-81-7; **2g** corresponding carbinol, 17334-08-6; **2h**, 119-61-9; **4a**, 53798-67-7; **4b**, 53798-68-8; **4c**, 41030-03-9; **4d**, 41030-01-7; **4e**, 53798-69-9; **4f**, 53798-70-2; **4g**, 53798-71-3; **4h**, 53798-72-4; **5a**, 53798-73-5; **5b**, 53798-74-6; **5c**, 41030-06-2; **5d**, 53798-75-7; **5e**, 53821-45-7; **5f**, 53798-76-8; **5g**, 53798-77-9; **5h**, 53798-78-0; **6a**, 20971-79-3; **6a** picrate, 53798-79-1; **6b**, 53798-80-4; **6b** picrate, 53798-81-5; **6c**, 53798-82-6; **6d**, 53798-83-7; **6e**, 53798-84-8; **6f**, 53798-85-9; **6g**, 53798-86-0; **6g** picrate, 53798-87-1; **6h**, 7746-94-3; 2-(1,3-dioxolan-2-yl)ethyl bromide, 18742-02-4; 1-methylimidazole, 616-47-7.

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Quinazolines and 1,4-Benzodiazepines. LXX.[1] *v*-Triazolo[1,5-*a*][1,4]benzodiazepines

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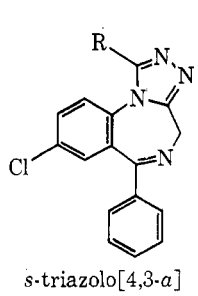
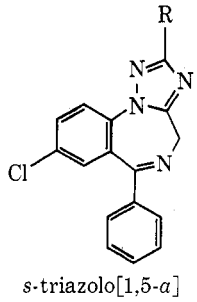
Recieved October 18, 1974

The cycloaddition reaction of 2-azido-5-chlorobenzophenone with dimethyl acetylenedicarboxylate provides 1-(2-benzoyl-4-chlorophenyl)-1*H*-1,2,3-triazole-4,5-dicarboxylic acid dimethyl ester. The oxime of this ketone undergoes reductive cyclization with zinc in acid which, together with subsequent transformations, give the first examples of the new tricyclic ring system named in the title.

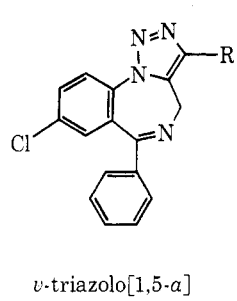
1,4-Benzodiazepines embellished with a triazole ring have been the subject of several recent reports in both the journal[2,3] and patent[4–7] literature. Compounds of types **1**[2–6] and **2**[7] are known compounds and represent the two possible ring systems in which an *s*-triazole ring is fused to the 1,2 positions of a 1,4-benzodiazepine. The third possible ring system of this type in which a *v*-triazole is so incorporated is exemplified in compounds **3** and **4**. A synthesis of such previously unknown compounds is the subject of this paper.



s-triazolo[4,3-*a*]
1

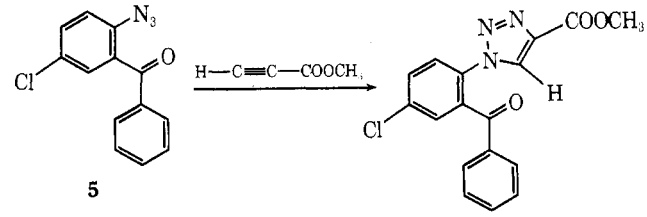


s-triazolo[1,5-*a*]
2



v-triazolo[1,5-*a*]
3, R = H
4, R = CH_3

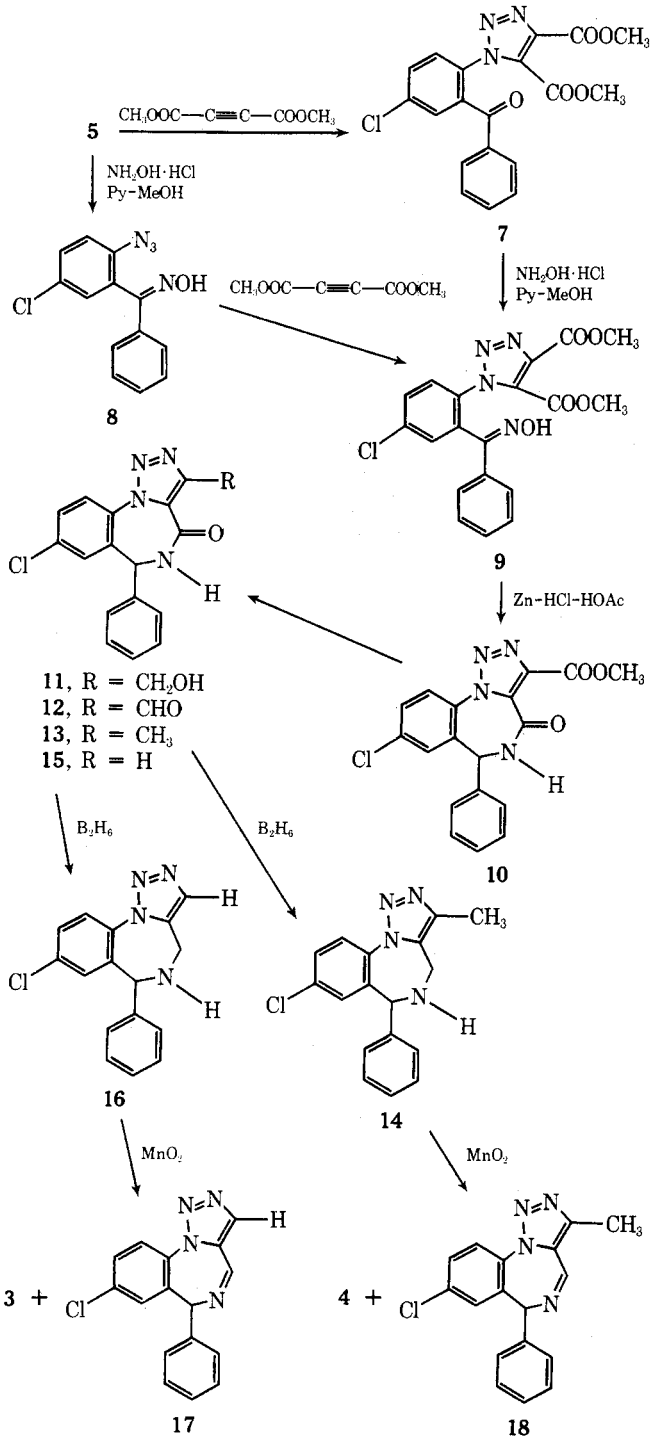
Of the several methods for the synthesis of *v*-triazoles,[8] the cycloaddition of acetylene derivatives to azides[9] appeared to be most applicable in the present instance, particularly since the appropriate azide **5** is readily accessible[10] from (commercially available) 2-amino-5-chlorobenzophenone. We initially anticipated a direct, essentially one-step synthesis of **3** by cycloaddition–condensation of propargyl amine with the azido ketone **5**. After numerous trials it became clear that a more reactive acetylene was necessary. Methyl propiolate reacts with **5** at room temperature to produce a single, crystalline adduct. However, while it was not clear from spectral data which of the two regiochemical modes of cycloaddition prevailed, our sustained inability to produce a tricyclic derivative from the adduct forced us to conclude that it has structure **6**. This result could have been predicted by analogy with the cycloaddition of phenyl azide and methyl propiolate in which the 1,4-disubstituted triazole is the major product (the 1,4 to 1,5 isomer ratio is approximately 7:1).[11]



5 **6**

This question of regiochemistry in the cycloadduct was simply avoided by using dimethyl acetylenedicarboxylate as the 1,3-dipolarophile. The resulting adduct **7** was converted to its oxime **9** and reductively cyclized to the lactam **10** as shown in Scheme I. Better yields of the cycloaddition

Scheme I



product **9** were obtained by first converting the azido ketone **5** to the azido oxime **8**.

Using compound **10** as the starting material, the series of υ-triazolobenzodiazepines **11**–**18** and the target compounds **3** and **4** were synthesized. Simultaneous reduction of both the amide and ester functions of **10** could be accomplished by prolonged exposure to $LiAlH_4$ in THF at reflux. However, since the chlorine atom was also lost to a large degree under these conditons, a stepwise reduction sequence leading through intermediates **11**–**14** was adopted. Excess sodium borohydride in boiling THF effected a selective reduction of the heterocyclic ester group.[12] Reoxidation to the aldehyde level with MnO_2 or CrO_3 afforded the aldehyde **12** and Wolff–Kishner[13] reduction of this substance to **13** completed a conversion of the "extra" ester function to a methyl group. In an alternative sequence, this "extra" ester function was removed completely by selective hydrolysis and thermal decarboxylation to give the lactam **15**.

Vigorous diborane reduction of the lactams **13** and **15** provided the secondary amines **14** and **16**. Oxidation of these dihydro-υ-triazolobenzodiazepines with MnO_2 produced in each case an isomeric pair of 4H and 6H compounds: **3** and **17** from **16**, and **4** and **18** from **14**. The separation of these isomeric products required recourse to column or preparative layer chromatography, but in all other reactions described, crystalline products were obtained directly following conventional work-up procedures.

Experimental Section[14]

2-Azido-5-chlorobenzophenone (5). A solution of 2-amino-5-chlorobenzophenone (232 g, 1 mol) in a mixture of acetic acid (500 ml), concentrated hydrochloric acid (200 ml), and water (300 ml) was cooled to 5° with an ice bath. A solution of sodium nitrite (75 g, 1.1 mol) in water (300 ml) was also cooled to 5° and then added to the first solution with stirring during the course of 10 min. A solution of sodium azide (71 g, 1.1 mol) in water (300 ml) was slowly added, during which the mixture foamed copiously. Stirring was continued for 30 min at 5° after completion of the addition and then kept for 1 hr without further cooling. The product was collected in two crops to give 227.1 g (88%) of crude azido ketone **5** as a light yellow solid after washing with water and air drying. A sample was recrystallized from petroleum ether to give colorless plates: mp 83–84°; ir (Nujol) 2150, 2120, and 1670 cm^{-1}.

Anal. Calcd for $C_{13}H_8ClN_3O$: C, 60.59; H, 3.13; N, 16.31. Found: C, 60.41; H, 3.13; N, 16.17.

1-(2-Benzoyl-4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylic Acid Methyl Ester (6). A solution of **5** (23.5 g) in excess methyl propiolate (50 ml) was kept for several days. Crops of the product were filtered off periodically, washed with ether, and air dried to give a total of 25.5 g (81.5%) of crude adduct in three crops. A sample was recrystallized from ether to give colorless crystals: mp 188–190°; ir (Nujol) 1735, 1680, 1620, 1545, and 1520 cm^{-1}; NMR ($CDCl_3$–DMSO-d_6) δ 3.80 (s, 3 H), 7.2–8.0 (m, 8 H), and 8.94 (s, 1 H); mass spectrum *m/e* 77 (100%), 105, 341 (M^+).

Anal. Calcd for $C_{17}H_{12}ClN_3O_3$: C, 59.75; H, 3.54; N, 12.30; Cl, 10.37. Found: C, 59.85; H, 3.64; N, 12.44; Cl, 10.45.

1-(2-Benzoyl-4-chlorophenyl)-1*H*-1,2,3-triazole-4,5-dicarboxylic Acid Dimethyl Ester (7). A solution of **5** (20 g) in excess dimethyl acetylenedicarboxylate (30 ml) was prepared with warming and kept for 3 days. The crystals which formed were collected, washed with cold ether, and dried in a vacuum oven to give 20.8 g (67%) of crude adduct. A sample was recrystallized from methanol to give colorless crystals: mp 125–126°; ir (Nujol) 1735, 1730, 1670, 1590, and 1575 cm^{-1}; NMR ($CDCl_3$) δ 3.85 (s, 3 H), 3.95 (s, 3 H), and 7.2–7.8 (m, 8 H); mass spectrum *m/e* 105 and 399 (M^+, 100%).

Anal. Calcd for $C_{19}H_{14}ClN_3O_5$: C, 57.08; H, 3.53; N, 10.51; Cl, 8.87. Found: C, 57.00; H, 3.41; N, 10.52; Cl, 8.90.

2-Azido-5-chlorobenzophenone Oxime (8). A mixture of **5** (231 g), excess hydroxylamine hydrochloride (240 g), and pyridine (500 ml) in methanol (2 l.) was stirred and heated under reflux for 3 hr. The condensor was removed periodically to permit loss of water with solvent vapor. The cooled mixture was concentrated under reduced pressure to ca. 750 ml and then partitioned between 2*N* HCl and ether. The ether layer was dried and concentrated to ca. 800 ml. Cyclohexane was added gradually to the boiling ether solution to induce crystallization. The product was collected in three crops, washed with cyclohexane, and vacuum dried at 55° to give 227.3 g (93%) of crude oxime as a pale yellow solid. A sample for analysis was recrystallized from ether–cyclohexane to give nearly colorless needles: mp 140–142° dec; ir (Nujol) 3250, 2140, 2110, and 1585 cm^{-1}; mass spectrum *m/e* 192 (100%), 272 (M^+).

Anal. Calcd for $C_{13}H_9ClN_4O$: C, 57.26; H, 3.33; N, 20.55; Cl, 13.00. Found: C, 57.50; H, 3.22; N, 20.62; Cl, 13.03.

1-[4-Chloro-2-(α-hydroxyimino)benzylphenyl]-1*H*-1,2,3-triazole-4,5-dicarboxylic Acid Dimethyl Ester (9). A. From Ketone 7. A mixture of ketone **7** (75.8 g), hydroxylamine hydrochloride (75.0 g), and pyridine (150 ml) in methanol (500 ml) was stirred and gently boiled for 4 hr. Additional methanol was added periodically to replace that which escaped as solvent vapor. After this time an additional 50 g of hydroxylamine hydrochloride and 20 ml of pyridine were added and the mixture was left at reflux overnight. TLC analysis showed the presence of some starting ma-

terial, wherefore a further addition of hydroxylamine hydrochloride (15 g) and pyridine (15 ml) was made and reflux continued for 4 hr. After cooling the solvent was removed under reduced pressure and the resulting concentrate partitioned between 2 *N* HCl and ether. The ether layer was dried, filtered through Celite, and evaporated to a yellow oil. This material crystallized from hot, aqueous methanol to give 35.2 g (44.8%) of the oxime **9** in two crops. The oxime prepared in this manner is a mixture of syn and anti isomers and shows two spots on TLC. An analytical sample was recrystallized from aqueous methanol to give colorless crystals: mp 129–131°; ir (Nujol) 3200, 1750, 1730, and 1575 cm^{-1}; NMR ($CDCl_3$) δ 3.6–4.0 (4 peaks, 6 H, OCH_3) and 7.2–7.8 (m, 8 H); mass spectrum *m/e* 77 (100%) and 414 (M^+).

Anal. Calcd for $C_{19}H_{15}ClN_4O_5$: C, 55.02; H, 3.65; N, 13.51; Cl, 8.54. Found: C, 54.97; H, 3.41; N, 13.33; Cl, 8.65.

B. From Azido Oxime 8. A solution of the azido oxime **8** (210.5 g) and excess dimethyl acetylenedicarboxylate (235 g) in ether (400 ml) was heated under reflux for 48 hr. Most of the ether was evaporated under reduced pressure and the residue was chilled. The product was collected, washed with 1:1 ether–cyclohexane, and air dried. Recrystallization from aqueous methanol gave 235.5 g (73%) of product in three crops of which the first (190 g) is a single isomer (one spot on TLC) and the second and third crops are syn–anti isomer mixtures. A sample of the first crop was recrystallized to give colorless crystals: mp 167–168°; ir (Nujol) 3200, 1750, 1730, and 1570 cm^{-1}; NMR ($CDCl_3$–DMSO-d_6) δ 3.74 (s, 3 H), 3.92 (s, 3 H), 7.2–7.8 (m, 8 H), and 11.5 (s, OH); mass spectrum *m/e* 77 (100%) and 414 (M^+).

Anal. Found: C, 55.02; H, 3.67; N, 13.43; Cl, 8.59.

8-Chloro-5,6-dihydro-4-oxo-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine-3-carboxylic Acid Methyl Ester (10). A mixture of oxime **9** (132 g, 0.318 mol) and zinc dust (100 g, 1.5 g-atoms) in glacial acetic acid (700 ml) was treated with 1 ml of concentrated HCl to initiate the reaction. Thereafter the stirred mixture was cooled to keep the temperature below 50°. After 2 hr, the remaining zinc was filtered out and washed several times with methylene chloride. The combined filtrate and washings were washed repeatedly with sodium carbonate solution until the acetic acid was removed. The organic layer was then dried and concentrated under reduced pressure until precipitation commenced. The concentrated solution was then diluted with twice its volume of ether, kept for 2 min, and then filtered to remove a dimeric by-product. The filtrate was kept overnight at room temperature and the lactam **10** collected, washed with ether, and air dried to give 54.2 g (46%) of colorless product. This isolation procedure was developed to avoid the need for column chromatography in isolating the desired lactam. A sample recrystallized from methylene chloride–methanol had mp 267–269°; ir (Nujol) 3150, 1735, 1685, and 1650 cm^{-1}; NMR (DMSO-d_6) δ 3.79 (s, 3 H), 5.85 (d, J = 7 Hz, 1 H), 6.9–8.1 (m, 8 H), and 9.87 (d, J = 7 Hz, NH); mass spectrum *m/e* 263 (100%) and 368 (M^+).

Anal. Calcd for $C_{18}H_{13}ClN_4O_3$: C, 58.62; H, 3.55; N, 15.19; Cl, 9.61. Found: C, 58.65; H, 3.55; N, 14.96; Cl, 9.59.

8-Chloro-5,6-dihydro-3-hydroxymethyl-4-oxo-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (11). A slurry of the lactam **10** (67.5 g, 0.183 mol) and sodium borohydride (50 g, 1.32 mol) in THF (2.5 l.) was stirred and heated under reflux for 10 hr. The solution was concentrated somewhat by evaporation under reduced pressure. Aqueous 2% HCl was added slowly to destroy excess hydride and the resulting mixture was partitioned between methylene chloride and water. The organic layer was dried and evaporated until the product began to separate. An equal volume of ether was added at this point and the solution chilled. The product was collected, washed with ether, and air dried to give 46.1 g (74%) of alcohol **11** as a colorless solid. A sample was recrystallized from methylene chloride to give colorless crystals: mp 218°; ir (Nujol) 3400, 3200, 3050, 1670, 1610, 1595, and 1575 cm^{-1}; NMR (DMSO-d_6) δ 4.56 (s, 2 H), 4.8 (broad, NH and OH), 5.74 (s, 1 H), and 6.9–8.0 (m, 8 H); mass spectrum *m/e* 217 (100%) and 340 (M^+).

Anal. Calcd for $C_{17}H_{13}ClN_4O_2$: C, 59.92; H, 3.85; N, 16.44; Cl, 10.40. Found: C, 59.90; H, 3.80; N, 16.64; Cl, 10.65.

8-Chloro-5,6-dihydro-3-formyl-4-oxo-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (12). A mixture of alcohol **11** (36.3 g) and activated manganese dioxide (405 g) in acetone (2 l.) was stirred at reflux for 6 hr and then overnight at room temperature. The solid was filtered out and thoroughly extracted several times with hot acetone. The combined filtrate and washings were evaporated to leave 15.4 g (42.5%) of aldehyde **12** as a colorless solid. This oxidation was also carried out on the same scale with chromium trioxide using the Ratcliffe and Rodehorst procedure[15] and gave the same yield.

A sample was recrystallized from ether–methanol to give crystals: mp 244–246°; ir (KBr) 3300 and 1660 cm^{-1}; NMR (DMSO-d_6) δ 5.90 (s, 1 H), 6.8–8.1 (m, 9 H, including NH), and 10.03 (s, 1 H); mass spectrum *m/e* 233 (100%) and 338 (M^+).

Anal. Calcd for $C_{17}H_{11}ClN_4O_2$: C, 60.28; H, 3.27; N, 16.54; Cl, 10.46. Found: C, 60.13; H, 3.43; N, 16.51; Cl, 10.41.

8-Chloro-5,6-dihydro-3-methyl-4-oxo-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (13). A solution of the aldehyde **12** (15.4 g) and 85% hydrazine hydrate (60 ml) in ethanol (300 ml) was heated on a steam bath for 2 hr. The solvent was removed under reduced pressure and the residue taken up in toluene (300 ml). Potassium *tert*-butoxide (15 g) was added and the mixture stirred and heated for 8 hr. The solvent vapors were allowed to escape for the first 15 min and heating thereafter was under reflux. The cooled mixture was washed with water (250 ml) and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried and evaporated. Recrystallization of the residue from methylene chloride–ether gave 13.4 g (91%) of the lactam **13** as colorless crystals: mp 248–250; ir (Nujol) 3170, 3050, 1665, and 1570 cm^{-1}; NMR ($CDCl_3$) δ 2.58 (s, 3 H), 5.55 (d, J = 6 Hz, s after D_2O exchange, 1 H), and 7.1–8.2 (m, 9 H, including NH); mass spectrum *m/e* 219 (100%) and 324 (M^+).

Anal. Calcd for $C_{17}H_{13}ClN_4O$: C, 62.87; H, 4.03; N, 17.25; Cl, 10.92. Found: C, 63.09; H, 4.17; N, 17.13; Cl, 10.90.

8-Chloro-5,6-dihydro-4-oxo-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (15). The lactam **10** (10.0 g) was taken up in excess 10% methanolic KOH and the solution kept at room temperature for 15 min, during which the potassium salt of the acid precipitated. The entire mixture was acidified with dilute HCl and the product collected and dried. The crude acid (8.6 g) was slurried in ethylene glycol (60 ml) and the mixture boiled for 5 min. After partitioning between water and methylene chloride, the organic layer was dried and evaporated to give 6.6 g (78%) of lactam **15.** An analytical sample prepared by vacuum sublimation at 195° had mp 248–249°; ir (Nujol) 3150, 3080, 1675, 1610, 1590, and 1550 cm^{-1}; NMR ($CDCl_3$–DMSO-d_6) δ 5.70 (d, J = 6 Hz, 1 H), 7.0–8.2 with singlet at 8.02 (9 H), and 9.51 (d, J = 6 Hz, NH); mass spectrum *m/e* 205 (100%) and 310 (M^+).

Anal. Calcd for $C_{16}H_{11}ClN_4O$: C, 61.84; H, 3.57; N, 18.03; Cl, 11.90. Found: C, 61.87; H, 3.53; N, 18.27; Cl, 11.53.

8-Chloro-5,6-dihydro-3-methyl-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (14). A solution of the lactam **13** (8.0 g) in THF (125 ml) was treated with 1 *M* diborane in THF (50 ml) and heated to reflux for 15 hr. Excess diborane was destroyed by addition of saturated aqueous Na_2SO_4 and the mixture partitioned between water and methylene chloride. The organic layer was dried and evaporated. The residue was triturated wth ether, filtered, and dried to give 6.1 g (80%) of the amine **14** as colorless solid. Recrystallization from methylene chloride–ether provided material with mp 161–163°. It was suitable for use as in the MnO_2 oxidation step but analyzed poorly and contained, in its infrared spectrum, an anomalous band at 2400 cm^{-1}. It may be an amine–borane complex. An analytically pure sample was prepared by boiling a solution of the product in methanol containing concentrated HCl for 10 min followed by work-up with aqueous NaOH and methylene chloride. The base from the organic layer was crystallized from ether–hexane, giving colorless crystals: mp 140–142°; ir (Nujol) 3300 and 1605 cm^{-1}; NMR ($CDCl_3$) δ 2.2 (broad, 1 H, NH), 2.50 (s, 3 H), 4.03 (AB q, J = 15 Hz, 2 H), 5.03 (s, 1 H), and 6.8–8.0 (m, 8 H); mass spectrum *m/e* 205 (100%) and 310 (M^+).

Anal. Calcd for $C_{17}H_{15}ClN_4$: C, 65.70; H, 4.86; N, 18.03; Cl, 11.41. Found: C, 65.79; H, 4.74; N, 18.13; Cl, 11.19.

8-Chloro-5,6-dihydro-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (16). The reduction of lactam **15** (5.4 g) with diborane was carried out as described for lactam **13** to give 3.6 g (70%) of the amine **16.** A sample recrystallized from methylene chloride–ether had mp 138–140°; ir (Nujol) 3200 and 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.18 (s, 1 H, NH), 4.12 (AB q, J = 15 Hz, 2 H), 5.00 (s, 1 H), and 6.8–8.0 (m, 8 H); mass spectrum *m/e* 191 (100%) and 296 (M^+).

A sample for analysis was vacuum sublimed.

Anal. Calcd for $C_{16}H_{13}ClN_4$: C, 64.76; H, 4.42; N, 18.88; Cl, 11.96. Found: C, 64.78; H, 4.36; N, 19.04; Cl, 11.89.

8-Chloro-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (3) and 8-Chloro-6-phenyl-6*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (17). A solution of the amine **16** (4.3 g) in methylene chloride (100 ml) was treated with activated manganese dioxide (25 g) and stirred under reflux for 2 hr. The solid was filtered out and

thoroughly washed with methylene chloride. The filtrate and washing were combined and evaporated to leave a colorless, crystalline mixture of two products (TLC). These were separated by column chromatography on 100 g of silica gel using methylene chloride as eluent. The 6H isomer **17**, 1.3 g (30%), was eluted first and then the more polar 4H isomer **3**, 1.2 g (28%), was obtained. A sample of compound **3** was vacuum sublimed at 140°, giving colorless crystals: mp 168–169°; ir (Nujol) 1620 and 1575 cm^{-1}; NMR ($CDCl_3$) δ 4.75 (s, 2 H) and 7.3–8.2 (m, 9 H); mass spectrum *m/e* 231, 265 (100%), and 294 (M^+).

Anal. Calcd for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.76; N, 19.00; Cl, 12.03. Found: C, 65.24; H, 3.82; N, 19.14; Cl, 12.09.

A sample of compound **17** was recrystallized from methylene chloride–ether to give colorless crystals: mp 123–125°; ir (Nujol) 1640 cm^{-1}; NMR ($CDCl_3$) δ 5.33 (broad s, 1 H), 6.83 (d, 1 H), 7.3–7.7 (m, 6 H), 7.90 (d, 1 H), 8.10 (s, 1 H), and 8.67 (broad s, 1 H); mass spectrum *m/e* 204, 238, 266, and 294 (100%, M^+).

Anal. Found: C, 65.49; H, 3.67; N, 19.22; Cl, 11.93.

8-Chloro-3-methyl-6-phenyl-4*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (4) and 8-Chloro-3-methyl-6-phenyl-6*H*-*v*-triazolo[1,5-*a*][1,4]benzodiazepine (18). The MnO_2 oxidation of amine **14** (3.6 g) under the conditions described above for amine **16** required 48 hr at reflux. The crude mixture of two products (3.0 g) was separated by chromatography on 15 preparative layer plates (silica gel with 5% CH_3OH in $CHCl_3$) giving 1.50 g (42%) of compound **4**, the more polar component, and 0.80 g (22%) of **18**.

A sample of compound **4** was recrystallized from methylene chloride–ether to give colorless crystals: mp 196–196.5°; ir (Nujol) 1620 cm^{-1}; NMR ($CDCl_3$) δ 2.42 (s, 3 H), 4.66 (s, 2 H), and 7.2–8.2 (m, 8 H); mass spectrum *m/e* 245, 279 (100%), and 308 (M^+).

Anal. Calcd for $C_{17}H_{13}ClN_4$: C, 66.13; H, 4.24; N, 18.15; Cl, 11.48. Found: C, 66.29; H, 4.46; N, 18.16; Cl, 11.36.

A sample of compound **18** recrystallized from ether had mp 133–135°; ir (Nujol) 1635 and 1555 cm^{-1}; NMR ($CDCl_3$) δ 2.53 (s, 3 H), 5.30 (d, J = 2 Hz, 1 H), 6.8–8.0 (m, 8 H), and 8.48 (d, J = 2 Hz, 1 H); mass spectrum *m/e* 203, 218, 252, 280 (100%), and 308 (M^+).

Anal. Found: C, 66.24; H, 4.22; N, 18.44; Cl, 11.81.

Registry No.—**3**, 53878-78-7; **4**, 53993-42-3; **5**, 53878-93-6; **6**, 53993-43-4; **7**, 53993-44-5; **8**, 53878-98-1; *syn*-**9**, 53993-45-6; *anti*-**9**, 53993-46-7; **10**, 53879-01-9; **11**, 53993-47-8; **12**, 53993-48-9; **13**, 53993-49-0; **14**, 53993-50-3; **15**, 53879-03-1; **16**, 53879-04-2; **17**, 53879-05-3; **18**, 53993-51-4; 2-amino-5-chlorobenzophenone, 719-59-5; methyl propiolate, 922-67-8; dimethyl acetylenedicarboxylate, 762-42-5; hydroxylamine hydrochloride, 5470-11-1.

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Nuclear Magnetic Resonance Studies on Conformations about the Nitrogen–Carbon Bond in Some *N*-Malonylimides and Some Comments on the Origin of Nitrogen–Nitrogen Bond Torsional Barriers

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Received September 4, 1974

The preparation and NMR studies of a series of *N*-malonyl derivatives of Diels–Alder adducts of anthracene–maleimide and anthracene–citraconimide have been described. In contrast to the tetraacylhydrazine systems, these compounds show no spectral multiplicities in their NMR signals at 44.5° owing to slow rate processes indicating that rotation about the N–C bond in these compounds is free on the NMR time scale. It has been further demonstrated that the nonbonding repulsion between the substituents is not the main contribution to the N–N bond torsional barriers in tetraacylhydrazine systems but that the lone-pair electronic interactions at the two nitrogen atoms are sufficiently effective. This is supported by preparing the sodium salts of the title compounds possessing a >N–$^-$C< system, isoeletronic with the N–N bond in tetraacylhydrazines which show multiplicity in their NMR spectra indicating hindered rotation about the N–C bond.

Studies on conformations by NMR spectroscopy have been receiving considerable attention during recent years.[1] Barriers to nitrogen inversion in cyclic hydrazines[2] and acyclic hydrazines[3] have been studied by dynamic NMR spectroscopy. Hindered inversion at the pyramidal nitrogen in aziridines has been rationalized[4] in terms of ring strain during inversion, while restricted rotation about the N–CO bonds has been assigned[5] to the partial double bond character of the amide bonds. High energy barriers to the inversion of *N,N'*-diacyltetrahydropyridazine of the type I (18–19 kcal/mol)[6] and the restricted rotation about the N–N bonds in tetraacylhydrazine systems of the type II and III[7] have been demonstrated by NMR spectroscopy and attributed largely to the nonbonding repulsions between the acyl substituents in the planar transition state. Existence of nonplanar conformations and high energy barriers to the N–N bond torsion in the *N,N'*-diacyl-*N,N'*-dialkylhydrazine system[8] (21–22 kcal/mol, the values fairly