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A novel and convenient synthesis of 1*H*-pyrrole-2,3,4,5-tetracarboxylates is described. Photocyclization of 1,1'-bis(methoxycarbonyl)divinylamine with acetylenedicarboxylates gave 7-azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylates **2a-i**, which on melting split ethylene off to yield 1*H*-pyrrole-2,3,4,5-tetracarboxylates **3a-i** quantitatively.

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Pyrroletetracarboxylates appeared often in the work of Nicolaus *et al.*, who identified the acid in the oxidation products of melanines. Several preparations of the carboxylates have been reported (1-7), which are not attractive, however, because of intricate steps or insufficient yield.

In the course of our work on the reaction of 1,1'-bis(methoxycarbonyl)divinylamine (BDA), we found that BDA reacted with acetylenedicarboxylates under irradiation to give 7-azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylates **2a-i**, which converted, on melting, into 1*H*-pyrrole-2,3,4,5-tetracarboxylates **3a-i** quantitatively (Scheme I).

diation to give 2,3-dihydropyrrole-2,5-dicarboxylate according to Chapman (10,11) and Wolff (12), which however failed.

In contrast, in the presence of acetylenedicarboxylate, BDA formed bicyclic 1:1-adduct **2a-i** with the carboxylate **1a-i** in a high yield. The products were identified by spectral data and elemental analyses. Such bicyclic system is known to split ethylene off to afford 5-membered heterocyclic compound, pyrrole-2,3,4,5-tetracarboxylate **3a-i** quantitatively in this case.

The present reaction provides a novel and convenient route for the preparation of pyrroletetracarboxylate.

Results and Discussion.

Irradiation products **2a-i** showed the elementary composition in accord with that of 1:1-adduct between BDA and acetylenedicarboxylates, as seen in Table 1. Mass spectra of **2a** and **2b** gave the molecular ion at *m/e* 327 and *m/e* 355, respectively, which also supported the products to be 1:1-adduct.

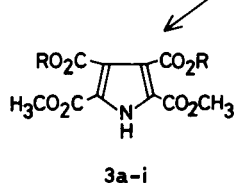
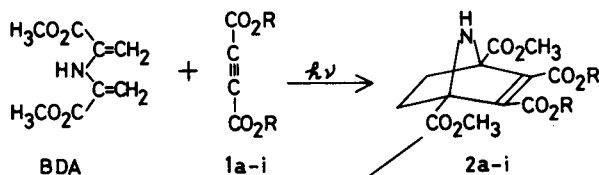
Chemical shifts and coupling constants in the range of 1.66-1.81 ppm and 2.28-2.42 ppm (Table 3) are identical with those characteristic of *endo* and *exo* ring protons at 5- and 6-positions of bicyclo[2.2.1]hept-2-ene (13,14) and 7-azabicyclo[2.2.1]hept-2-ene ring systems (15-17). From the above analyses together with the existence of double bond in ir (Table 2), the novel products **2a-i** in this work must have the proposed bicyclic structure.

Thermal degradation of the compounds **2a-i** yielded the corresponding **3a-i**, the structure of which were determined by elemental analyses (Table 1), ir, uv (Table 2) and nmr (Table 4) analyses.

Comparison with data in literatures also supports the proposed structure **3a-i**; *eg* melting point of tetramethyl-ester (1,2) and characteristic absorptions of pyrroletetracarboxylates in ir (18,19) and uv (20) spectra.

It has been already reported (17,21) that 7-azabicyclo[2.2.1]heptenes split readily ethylene off on heating. The present thermal degradation seems to be the same, since

SCHEME I



Compound No.	R
a	CH ₃
b	CH ₂ CH ₃
c	CH ₂ CH ₂ CH ₃
d	CH(CH ₃) ₂
e	CH ₂ (CH ₂) ₂ CH ₃
f	CH(CH ₃)CH ₂ CH ₃
g	C(CH ₃) ₃
h	CH ₂ (CH ₂) ₃ CH ₃
i	C ₆ H ₁₁

BDA, which can be prepared by the base catalyzed reaction of methyl β-halo-α-aminopropionate hydrohalide (**8**), behaves as a cross-conjugated dienamine (**9**). Therefore, it was expected to undergo electrocyclic reaction under irra-

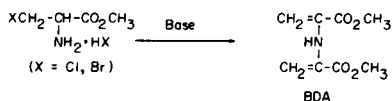


Table 1

7-Azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylates, **2a-i** and Pyrrole-2,3,4,5-tetracarboxylates, **3a-i**

Compound No.	R	Mp °C	Yield %	Recrystallization solvents (a)	Formula	Analyses					
						Calcd., %			Found, %		
						C	H	N	C	H	N
2a	CH ₃	89	93	C	C ₁₄ H ₁₇ NO ₈	51.38	5.20	4.28	51.20	5.09	4.35
2b	CH ₂ CH ₃	syrup	91	—	C ₁₅ H ₂₁ NO ₈	54.08	5.92	3.49	54.10	6.02	3.79
2c	CH ₂ CH ₂ CH ₃	syrup	90	—	C ₁₆ H ₂₅ NO ₈	56.40	6.53	3.66	56.54	6.71	3.95
2d	CH(CH ₃) ₂	58	91	E-H	C ₁₈ H ₂₅ NO ₈	56.40	6.53	3.66	56.44	6.81	3.86
2e	CH ₂ (CH ₂) ₂ CH ₃	syrup	90	—	C ₂₀ H ₂₉ NO ₈	58.39	7.06	3.41	58.50	6.96	3.16
2f	CH(CH ₃)CH ₂ CH ₃	syrup	86	—	C ₂₀ H ₂₉ NO ₈	58.39	7.06	3.41	58.11	6.89	3.12
2g	C(CH ₃) ₃	124	84	E	C ₂₀ H ₂₉ NO ₈	58.39	7.06	3.41	58.38	7.14	3.28
2h	CH ₂ (CH ₂) ₃ CH ₃	syrup	82	—	C ₂₂ H ₃₃ NO ₈	60.14	7.52	3.19	59.85	7.32	3.38
2i	C ₆ H ₁₁	74	81	C	C ₂₄ H ₃₃ NO ₈	62.20	7.13	3.02	62.17	7.31	3.03
3a	CH ₃	124-125 (b)	98	E	C ₁₂ H ₁₃ NO ₈	48.16	4.35	4.68	48.01	4.46	4.62
3b	CH ₂ CH ₃	125-126	90	E	C ₁₄ H ₁₇ NO ₈	51.38	5.20	4.28	51.19	5.32	4.43
3c	CH ₂ CH ₂ CH ₃	94	91	E	C ₁₆ H ₂₁ NO ₈	54.08	5.92	3.94	53.90	5.97	4.05
3d	CH(CH ₃) ₂	113-114	99	E-H	C ₁₈ H ₂₁ NO ₈	54.08	5.92	3.94	54.20	6.18	3.69
3e	CH ₂ (CH ₂) ₂ CH ₃	74	93	E-H	C ₁₈ H ₂₅ NO ₈	56.40	6.53	3.66	56.54	6.13	3.59
3f	CH(CH ₃)CH ₂ CH ₃	78	90	EE-H	C ₁₈ H ₂₅ NO ₈	56.40	6.53	3.66	56.44	6.49	3.68
3g	C(CH ₃) ₃	127	98	E-H	C ₁₈ H ₂₅ NO ₈	56.40	6.53	3.66	56.39	6.68	3.61
3h	CH ₂ (CH ₂) ₃ CH ₃	54-55	93	E-H	C ₂₀ H ₂₉ NO ₈	58.39	7.06	3.41	58.62	7.16	3.29
3i	C ₆ H ₁₁	163-164	98	E	C ₂₂ H ₂₉ NO ₈	60.69	6.67	3.22	60.66	6.92	3.23

(a) C = carbon tetrachloride, E = ethanol, H = hexane, EE = ethyl ether. (b) Mp 124-125° (from carbon tetrachloride) (1,2).

Table 2

IR and UV Spectral Data of 7-Azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylates, **2a-i** and Pyrrole-2,3,4,5-tetracarboxylates, **3a-i**

Compound No.	IR Spectra, cm ⁻¹ (potassium bromide)			UV Spectra, (carbon tetrachloride) nm λ max (log ε max)		3e	3470, 3290	1745, 1735, 1695	223 (4.16) 267 (4.02)
	NH	C=O	C=C						
2a	3250	1740, 1710	1640	254 (3.27)		3f	3450, 3270	1740, 1730, 1690	223 (4.19) 267 (4.06)
2b (a)	3250	1740, 1720	1640	262 (3.47)		3g	3460, 3280	1741, 1729, 1695	223 (4.22) 269 (4.14)
2c (a)	3300	1750, 1730	1635	263 (3.46)		3h	3460, 3270	1745, 1734, 1695	225 (4.16) 267 (4.07)
2d	3310	1760, 1740	1635	262 (3.32)		3i	3460, 3270	1742, 1732, 1695	224 (4.28) 267 (4.19)
2e (a)	3310	1760, 1730	1640	262 (3.28)					
2f (a)	3300	1760, 1720	1640	262 (3.32)					
2g	3380	1750, 1720	1622	262 (3.27)					
2h (a)	3300	1740, 1720	1630	262 (3.42)					
2i	3300	1750, 1720	1635	263 (3.45)					

(a) Measured in neat liquid film. (m) Medium. (w) Weak. (sh) Shoulder. (s) Strong.

the cloven ethylene was captured as its dibromide.

This work provides a novel and useful synthesis of 1*H*-pyrrole-tetracarboxylates.

EXPERIMENTAL

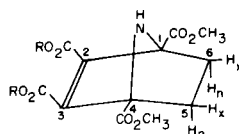
The nmr spectra were recorded on a Jeol JNM-PS-100 spectrometer using TMS as an internal standard. The ir spectra were taken on a Hitachi EPI-G3 or JASCO J-0033 spectrophotometer. The uv spectra were recorded using Shimadzu double beam spectrophotometer UV-200. Mass spectra were obtained on a Finnigan 3300E GC-MS spectrometer. All boiling and melting points were uncorrected.

1,1'-Bis(methoxycarbonyl)divinylamine (BDA).

This compound was prepared by the base catalyzed reaction of methyl β-halo-α-aminopropionate hydrohalide (**8**), mp 51-51.5° (from ethanol); nmr (carbon tetrachloride): δ 3.81 (s, 6H), 5.01 (bs, 2H), 5.50 (bs, 2H), 7.28 (b, 1H); ir (potassium bromide): 3350 (NH), 1720 (C=O), 1620 cm⁻¹ (C=C); uv (carbon tetrachloride): λ max 282 (ε, 5399), 301 nm (ε, 5466).

Compound No.	IR Spectra, cm ⁻¹ (carbon tetrachloride)				UV Spectra, nm (Ethanol) λ max (log ε max)
	NH (m) (w)	C=O (sh) (s)		(sh)	
3a	3440, 3270	1745, 1728, 1690		226 (3.85) 268 (3.81)	
3b	3470, 3290	1750, 1738, 1695		224 (3.87) 267 (3.80)	
3c	3460, 3280	1749, 1737, 1695		224 (3.89) 267 (3.81)	
3d	3460, 3280	1743, 1734, 1695		225 (4.15) 267 (4.13)	

Table 3

¹H-NMR Spectral Data of 7-Azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylates (a)

Compound No.	Chemical Shifts (b), (c) of Ring Protons and of Methyl Protons in Methyl Esters
2a-i	H _n (C-5 and C-6) 1.66 (dd) -1.81 (dd) (J _{5n,6x} = J _{5x,6n} = 4.5 Hz, J _{5n,5x} = J _{6n,6x} = 11.3 Hz)
	H _x (C-5 and C-6) 2.28 (dd) -2.42 (dd)
	NH (d) 2.79 (br) -2.87 (br)
	CO ₂ CH ₃ (C-1 and C-4) 3.76 (s) -3.83 (s)

Compound No.	R	Chemical Shifts (c) of Substituent's Protons in Esters on C-2 and C-3
2a	CH ₃	3.80 (s)
2b	CH ₂ CH ₃	1.31 (t), 4.25 (qa)
2c	CH ₂ CH ₂ CH ₃	0.96 (t), 1.70 (sx), 4.15 (t)
2d	CH(CH ₃) ₂	1.29 (du), 5.05 (sp)
2e	CH ₂ (CH ₂) ₂ CH ₃	0.94 (t), 1.21-1.74 (m), 4.19 (t)
2f	CH(CH ₃)CH ₂ CH ₃	0.91 (t), 1.26 (du), 1.60 (qi), 4.93 (sx)
2g	C(CH ₃) ₃	1.48 (s)
2h	CH ₂ (CH ₂) ₃ CH ₃	0.92 (t), 1.24-1.74 (m), 4.16 (t)
2i	C ₆ H ₁₁	1.12-2.06 (m), 4.87 (bs)

(a) Spectra are recorded in deuteriochloroform. Chemical shifts are given in δ . Integration of peak areas was consistent with assigned structure in each case. (b) Depending on the difference of the bicyclic systems **2a-i**, chemical shifts of these protons appear in the region of the assigned δ values. (c) The abbreviations employed are conventional, s = singlet, du = doublet, t = triplet, qa = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, br = broad, bs = broad singlet, dd = doublet. (d) Exchangeable with deuterium oxide.

Acetylenedicarboxylate, **1a-i** (22).

These diesters were prepared according to the published methods, boiling points, °C/mm Hg [literature °C/mm Hg]: **1a**, 94.5-95/18 [(23), 95-98/19]; **1b**, 114-115/18 [(23), 96-98/8]; **1c**, 116/6 [(24), 116/5]; **1d**, 103/7 [(24), 96/3]; **1e**, 121-122/3 [(24), 139/5]; **1f**, 86/0.2; **1g**, 50/0.54 [(25), mp 35-36°C]; **1h**, 128/0.3 [(24), 143/1.5]; **1i**, 137/0.1.

Preparation of 7-Azabicyclo[2.2.1]hept-2-ene-1,2,3,4-tetracarboxylate, **2a-i**.

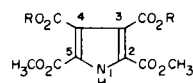
A solution of BDA (0.005 mole) and acetylenedicarboxylate (0.02 mole) in carbon tetrachloride (30 ml) was irradiated by a 100W high pressure mercury lamp under nitrogen atmosphere at $18 \pm 2^\circ$. The reaction was monitored by hplc.

After irradiation for 2-3 hours in a 35 ml cylindrical Pyrex vessel, the solvent was evaporated *in vacuo*, leaving a solid or syrup residue. The resulting solid was purified by recrystallization from the appropriate solvent, whereas the syrup was purified by elution on silica gel with chloroform. Results are listed in Table 1, ir and uv data in Table 2, nmr in Table 3.

Preparation of 1*H*-Pyrrole-2,3,4,5-tetracarboxylate, **3a-i** Through Cleavage of Ethylene.

In a 25 ml two-necked flask, fitted with an inlet of nitrogen and a gas-

Table 4

¹H-NMR Spectral Data of Pyrrole-2,3,4,5-tetracarboxylates (a)

Compound No.	R	Chemical Shifts (b) of Substituent's Protons in Esters on C-3 and C-4
3a	CH ₃	3.89 (s)
3b	CH ₂ CH ₃	1.35 (t), 4.33 (qa)
3c	CH ₂ CH ₂ CH ₃	0.98 (t), 1.72 (sx), 4.17 (t)
3d	CH(CH ₃) ₂	1.36 (d), 5.22 (sp)
3e	CH ₂ (CH ₂) ₂ CH ₃	0.95 (t), 1.26-1.84 (m), 4.27 (t)
3f	CH(CH ₃)CH ₂ CH ₃	0.95 (t), 1.30 (du), 1.62 (qi), 4.99 (sx)
3g	C(CH ₃) ₃	1.58 (s)
3h	CH ₂ (CH ₂) ₃ CH ₃	0.91 (t), 1.22-1.76 (m), 4.22 (t)
3i	C ₆ H ₁₁	1.14-2.16 (m), 5.04 (bs)

Compound No. Chemical Shifts (b), (c) of Methyl Protons in Methyl Esters and of Ring Proton

3a-i	CO ₂ CH ₃ (C-2 and C-5)	3.85 (s) -3.93 (s)
	NH (d)	10.19 (br) -10.40 (br)

(a) Spectra are recorded in deuteriochloroform. Chemical shifts are given in δ . Integration of peak areas was consistent with assigned structure in each case. (b) The abbreviations employed are conventional, s = singlet, du = doublet, t = triplet, qa = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, br = broad, bs = broad singlet. (c) Depending on the difference of the pyrrole system **3a-i**, chemical shifts of these protons appear in the region of the assigned δ values. (d) Exchangeable with deuterium oxide.

outlet tube connected to a gas-absorption trap, was placed **2a-i** (0.005 mole), which was heated in an oil bath at 90-120° under a stream of nitrogen. The exhausted gas was lead into a solution of bromine in carbon tetrachloride and the resulting ethylene dibromide was identified. After heating for 3-4 hours, when the liberation of ethylene ceased, the reaction mixture was cooled to room temperature and the resulting solid was recrystallized. Physical properties and analytical data of products **3a-i** are listed in Table 1, ir and uv data in Table 2, and nmr in Table 4.

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