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Syntheses of Trispirocyclopropanes *via* Triple Photodecarbonylations of Polymethyleneketene Trimers[1]

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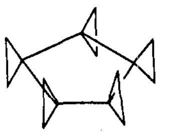
Trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (**5**, $n = 5$), trispiro[5.1.5.1.5.1]heneicosane-7,14,21-trione (**5**, $n = 6$), and trispiro[6.1.6.1.6.1]tetracosane-8,16,24-trione (**5**, $n = 7$) undergo triple photodecarbonylation when exposed to ultraviolet irradiation of wavelength greater than 258 nm. The resulting solid hydrocarbons trispiro[4.0.4.0.4.0]pentadecane (**4**, $n = 5$), trispiro[5.0.5.0.5.0]octadecane (**4**, $n = 6$), and trispiro[6.0.6.0.6.0]heneicosane (**4**, $n = 7$) were isolated in 14.1, 4.2, and 1.6% yields, respectively. Trispiro[5.0.5.0.5.0]octadecane could also be obtained *via* acetone photosensitization of trimer **5** ($n = 6$). The monodecarbonylated cyclopentane-1,3-diones **7**, **8**, **10**, and **13** and the trispiro cyclobutanones **9** and **12** have been isolated and characterized. In the case of trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (**5**, $n = 4$), irradiation in pentane yielded the δ lactone **6** (30%) and trispiro[3.1.3.1.3.0]tetradecane-5,10-dione (**7**) (11.4%). The effect of ring size in leading to the observed photolysis products is briefly discussed.

The synthesis of pentaspiro[2.0.2.0.2.0.2.0.2.0]pentadecane (**1**) has been described by Ripoll and Conia.[4] This was the first report of this type of polyspiro system and the general name "rotane" was suggested because of the paddlewheel-like arrangement of the outer cyclopropane rings. The syntheses of tetraspiro[5.0.2.0.5.0.2.0]octadecane (**2**)[5] and trispiro[2.0.2.0.2.0.2.0]dodecane (**3**)[6] were subsequently reported. As part of a program in the synthesis of paddlewheel systems with a central three-membered ring **4** (n = 4, 5, 6, 7), the photochemical behavior of polymethyleneketene trimers was studied. The choice of trimers **5** (n = 4, 5, 6, 7) was founded on the expectation that a stepwise triple photodecarbonylation[7] would occur to give the trispiro cyclopropanes. These expectations were partially realized.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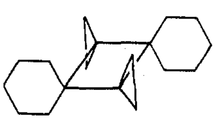
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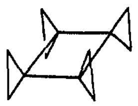
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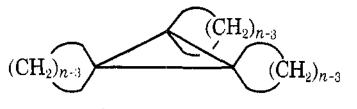
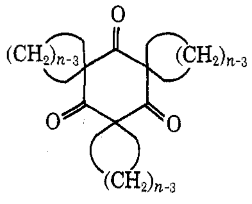


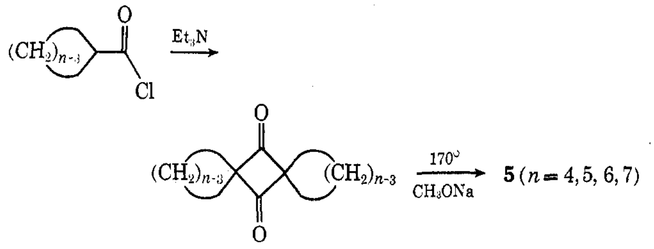
4 (n = 4,5, 6, or 7)



5 (n = 4,5,6, or 7)

The trimers **5** (n = 4, 5, 6, 7) have been prepared previously from the appropriately substituted 1,3-cyclobutanediones[9,10] by a base-catalyzed process. The 1,3-cyclobutanediones are readily obtained from the dehydrohalogenation of the corresponding cycloalkanecarbonyl chlorides with triethylamine. The syntheses of trimers **5** (n = 4, 5, 6, 7) are represented in Scheme I.

SCHEME I



All irradiations were conducted in dilute pentane or acetone solutions using a 450-W Hanovia high-pressure broad-spectrum mercury-vapor lamp. A Pyrex (ab-

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(1) Part of this material was reported in preliminary form: see A. P. Krapcho and F. J. Waller, *Tetrahedron, Lett.*, 3521 (1970).

(2) Abstracted in part from the Ph.D. Thesis submitted to the University of Vermont, 1970.

(3) National Aeronautics and Space Administration Trainee, 1968–1970.

(4) (a) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1969); (b) J. L. Ripoll, J. C. Limasset, and J. M. Conia, *Tetrahedron*, **27**, 2431 (1971).

(5) A. P. Krapcho and D. E. Horn, *Tetrahedron Lett.*, 4537 (1969).

(6) (a) J. M. Conia and J. M. Denis, *ibid.*, 3545 (1969); (b) P. Le Perchec and J. M. Conia, *ibid.*, 1587 (1970).

(7) A small yield of hexamethylcyclopropane has been reported by Hostettler in the photolysis of hexamethylcyclohexane-1,3,5-trione.[8]

(8) H. U. Hostettler, *Tetrahedron Lett.*, 1941 (1965).

(9) J. L. Erickson, F. E. Collins, Jr., and B. L. Owen, *J. Org. Chem.*, **31**, 480 (1966).

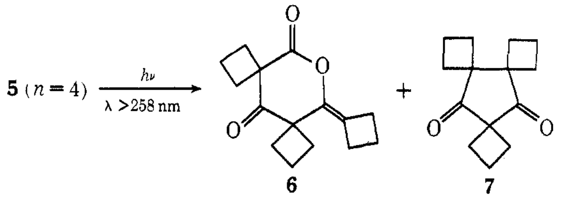
(10) M. Regitz and J. Ruter, *Chem. Ber.*, **102**, 3877 (1969).

solute cutoff at 280 nm) or Corex filter (absolute cutoff at 258 nm) was employed to assure that the initial excitation was restricted to the n–π* band of the chromophore. The photolyses were followed by withdrawal of small aliquots at periodic intervals and analyzing for the disappearance of the characteristic trimer carbonyl band (see Experimental Section) by infrared spectroscopy.

Results

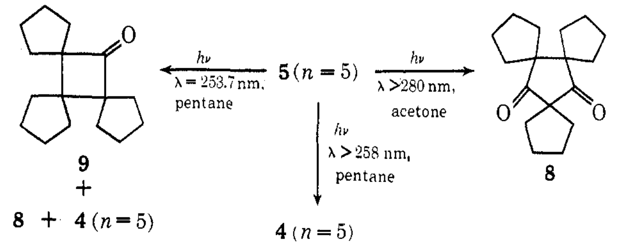
Trispiro[3.1.3.1.3.1]pentadecane-5,10,15-trione (5, n = 4).—Irradiation of a 0.016 M pentane solution of **5** (n = 4) using Corex optics for 1 hr led to two new products besides an insoluble solid and a small amount of starting material. The two new products, **6** (30.0%) and **7** (11.4%), were isolated by preparative scale vpc. The elemental analysis of **6** indicated that it was isomeric with **5** (n = 4). Pertinent infrared bands at 1715 (C=O) and 1765 cm^{-1} [C–C(=O)–O–C] and two strong bands at 1280 and 1085 cm^{-1} (CO) were characteristic of **6**. In addition, the δ lactone was rearranged by base catalysis[11] to trimer **5** (n = 4) in 59.2% yield. This spectroscopic and chemical data is consistent with the δ lactone assignment. The isomeric δ lactone upon further irradiation under identical conditions for **5** (n = 4) led to an uncharacterized solid.

The second photoproduct **7** analyzed for $C_{14}H_{18}O_2$, indicating that a molecule of carbon monoxide had been lost. On the basis of infrared carbonyl absorptions[13] at 1715 (C=O) and 1755 cm^{-1} (C=O) and its nmr spectrum displaying a pattern consistent with the cyclobutyl rings being intact, the photoproduct was assigned the structure trispiro[3.1.3.1.3.0]tetradecane-5,10-dione (**7**). No substituted cyclobutanone or hydrocarbon could be detected under the above experimental conditions.



Trispiro[4.1.4.1.4.1]octadecane-6,12,18-trione (5, n = 5).—When irradiated with ultraviolet light of wavelength above 258 nm for 3 hr, a 0.01 M pentane solution of trione **5** (n = 5) underwent triple photodecarbonylation. The solid hydrocarbon, $C_{15}H_{24}$, was isolated in 10% yield and exhibited infrared bands at 2955, 2865, and 1455 cm^{-1} and a molecular weight of 204 (mass spectrum). The nmr spectrum indicated that bond ruptures of the cyclopentyl rings did not occur. These spectroscopic data are consistent with the structure trispiro[4.0.4.0.4.0]pentadecane (**4**, n = 5).

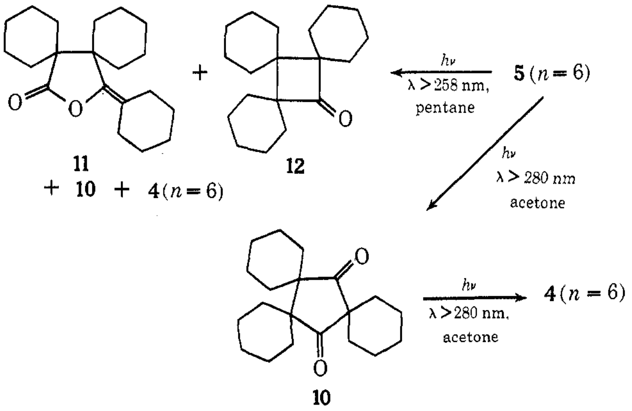
Utilizing ultraviolet irradiation at 253.7 nm,[14] a 0.014 M pentane solution of **5** (n = 5) after 65 hr yielded two photolabile intermediates, **8** (7%) and **9** (8%). Compound **8** gave an elemental analysis for $C_{17}H_{24}O_2$ and exhibited pertinent carbonyl infrared absorptions[13] at 1715 and 1750 cm^{-1}, while compound **9** possessed a ketone infrared band at 1755 cm^{-1} and analyzed for $C_{16}H_{24}O$. Again nmr spectra for **8** and **9** were in accord with noncyclopentyl ring rupture. The above information is consistent for trispiro[4.1.4.1.4.0]heptadecane-6,12-dione and trispiro[4.1.4.0.4.0]hexadecan-6-one, respectively. A longer irradiation time, 79.5 hr, gave a 14.1% yield of hydrocarbon **4** (n = 5) isolated by preparative vpc.



Employing acetone[15] as photosensitizer (E_T = 79 kcal/mol, Φ = 1)[16] and Pyrex-filtered light, a 32.6% yield of **8** was obtained after 12.5 hr of irradiation.

Trispiro[5.1.5.1.5.1]heneicosane-7,14,21-trione (5, n = 6).—Photolysis of a 2.1 × 10^{-3} M pentane solution of **5** (n = 6) for 12 hr using a Pyrex filter led to a 51.0% isolation of a solid. The solid, with carbon–hydrogen analysis for $C_{20}H_{30}O_2$, showed infrared bands[13] at 1705 and 1745 cm^{-1}. Likewise, the nmr spectrum did not show any evidence of cyclohexyl ring rupture. This evidence supports the trispiro[5.1.5.1.5.0]eicosane-7,14-dione (**10**) structure. Using acetone[15] as a photosensitizer and a Pyrex filter, a 66% yield of **10** could be isolated after 12 hr of irradiation.

However, when a Corex filtering system was utilized, a 0.015 M pentane solution when photolyzed for 89.5 hr afforded 15.2% of **10** in addition to two new photoproducts **11** (3.2%) and **12** (1.2%) and hydrocarbon **4** (n = 6). Photoproduct **11** was isomeric with **10** and showed infrared bands at 1780 (C=O) and 1680 cm^{-1} (C=C) and a nmr spectrum which displayed a broad four-proton envelope centered at δ 2.30. From these characteristics, the structure was assigned as lactone **11**. The other photoproduct possessed an infrared



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[11] Clark[12] has reported the formation of hexamethylcyclohexane-1,3,5-trione from the sodium methoxide catalyzed thermal rearrangement of 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic δ-lactone.

[12] R. D. Clark, *J. Org. Chem.*, **32**, 399 (1967).

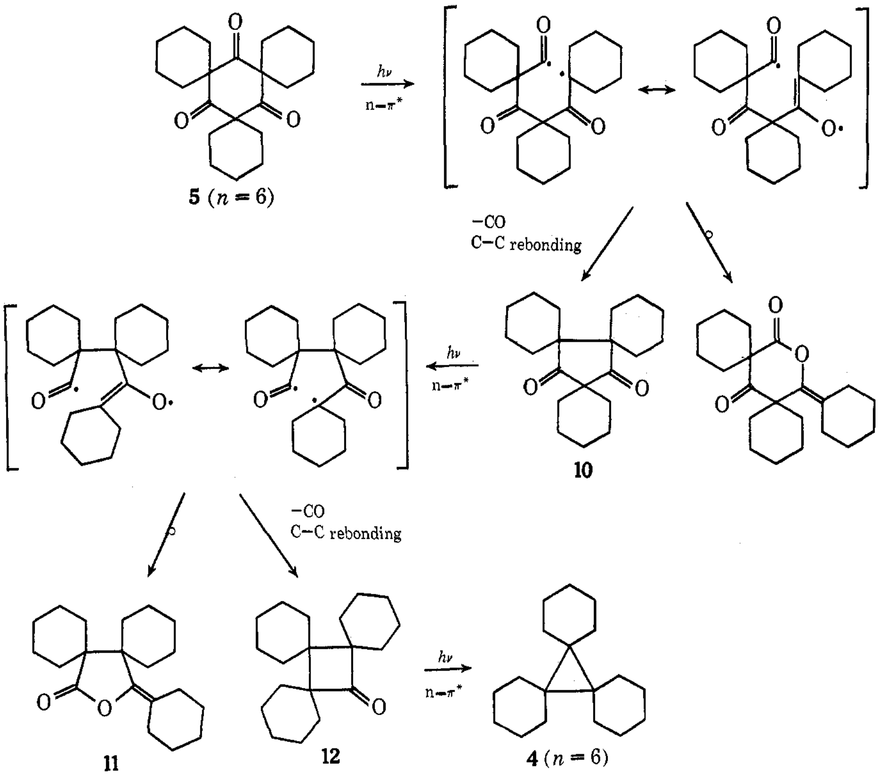
[13] The two absorption bands in the carbonyl region are apparently characteristic of 2,2-substituted 1,3-cyclopentanedione systems. The carbonyl band at higher frequency is more intense than the band at lower frequency. For discussion of two ir bands in the region around 1700 cm^{-1} see O. H. Mattsson and C. A. Wachtmeister, *Acta Chem. Scand.*, **22**, 79 (1968).

[14] A Rayonet RPR-100 chamber reactor fitted with 16 RPR-253.7 nm lamps was used as a light source.

[15] The acetone absorbed >99% of the light.

[16] N. J. Turro, J. C. Dalton, and D. S. Weiss in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, pp 8–13.

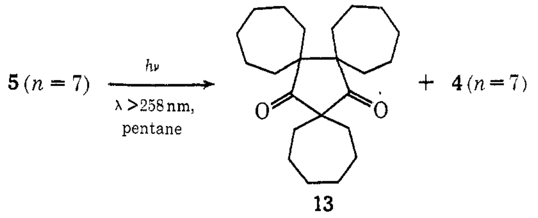
SCHEME II



absorption at 1750 cm^{-1} and was assigned as trispiro[5.1.5.0.5.0]nonadecan-7-one (**12**).

The solid hydrocarbon, $C_{18}H_{30}$, gave a simple infrared spectrum with bands at 2980, 2925, 2855, and 1445 cm^{-1}. The nmr spectrum displayed a broad singlet at 1.47 ppm. This hydrocarbon, trispiro[5.0.5.0.5.0]octadecane (**4**, *n* = 6), was obtained in ~1% yield.[17] The same yield of **4** (*n* = 6) was obtained in the acetone photosensitization of trispiro[5.1.5.1.5.0]eicosane-7,14-dione (**10**).[15]

Trispiro[6.1.6.1.6.1]tetracosane-8,16,24-trione (5, *n* = 7).—Similarly, when a 0.022 *M* pentane solution of **5** (*n* = 7) was irradiated with light of wavelength greater than 258 nm for 6 hr, two products, **13** (19.0%) and **4** (*n* = 7) (1.6%), were isolated. Photoproduct **13** gave analysis consistent for the loss of 1 mol of carbon monoxide, $C_{23}H_{36}O_2$, and pertinent infrared bands[13] at 1715 and 1750 cm^{-1}. The nmr spectrum showed a broad envelope centered at 1.63 ppm. Compound **4** (*n* = 7) was a solid hydrocarbon, $C_{21}H_{36}$, with characteristic infrared bands at 2910, 2855, and 1460 cm^{-1} and a broad singlet at 1.57 ppm in the nmr spectrum.



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Hexamethylcyclohexane-1,3,5-trione.—In order to compare our results with those of Hostettler,[8] a 0.014 *M* pentane solution of hexamethylcyclohexane-1,3,5-trione was irradiated for 4 hr with ultraviolet light of wavelength greater than 280 nm. Examination of the photolysate by infrared showed the trione still present and hexamethylcyclopentane-1,3-dione as the major product. The major product was isolated by preparative vpc in 48.0% yield and had identical physical properties with those described by Hostettler.[8] Sensitization by acetone[15] led to unchanged hexamethylcyclohexane-1,3,5-trione.

Discussion

The above experimental results clearly show that the photochemical behavior of the polymethyleneketene trimers is synthetically useful in the preparation of rotanes with a central three-membered ring.

The hexamethylcyclohexane-1,3,5-trione and triones **5** (*n* = 5, 6, 7) behave differently from trione **5** (*n* = 4). However, all have in common the same structural feature, a cyclic nonenolizable 1,3,5-triketone moiety. The mechanism which best describes the photochemical transformation of triones **5** (*n* = 4, 5, 6, 7) is depicted by **5** (*n* = 6) in Scheme II.[8] The photoexcitation of the carbonyl (n–π*) results in the fission of the C–C bond (α cleavage giving a C,C diradical). In the case of trione **5** (*n* = 4), the major photoproduct is the δ lactone resulting *via* a mesomeric C,O diradical. This is in line with the fact that cycloalkyl radicals[18] are stable in the sequence $C_7 > C_5 > C_6 \gg C_4$.[19] Furthermore, trispiro[5.1.5.1.5.0]eicosane-7,14-dione also afforded an isomeric lactone which reflects the cyclohexyl radical instability and subsequent rearrangement *via* a mesomeric C,O

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[17] An uninterrupted irradiation of trione **5** (*n* = 6) for 90.5 hr afforded 4.2% of **4** (*n* = 6). The effect of oxygen on the overall yield of **4** (*n* = 6) was not investigated.

[18] A formal analogy of photochemical reaction processes to free radical reactions initiated by other sources exists. H. Brown and coworkers predicted, based on I-strain hypothesis, that homolysis to form a free radical on a ring position follows the order 5 > 7 > 6 > 4. See H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).

[19] C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *ibid.*, **75**, 2078 (1953).

TABLE I

PROPERTIES AND SPECTRAL DATA FOR THE TRISPIROCYCLOHEXANE-1,3,5-TRIONES

5, *n*	Mp or bp, °C (mm)	Uv (CH_3OH), nm (ε)	Nmr ($CDCl_3$), δ
4	108–110 (0.07)^{a}	244 (218)	2.3–3.0 (12 H, m)
		303 (162)	1.7–2.3 (6 H, m)
5	112–114^{b}	224 (535)	1.5–2.45 (m)
		291 (135)	
6	144–146^{c}	230 (467)	1.78, 1.68, and
		295 (128)	1.55 (broad envelopes)
7	127–128^{d}	235 (281)	1.95 (12 H, broad envelope)
		300 (85)	1.60 (24 H, broad envelope)

^{a} Reference 9, bp 139–140° (2.0 mm). ^{b} Reference 9, mp 112.5–113.5°. ^{c} Reference 9, mp 147°. ^{d} Reference 10, mp 127°.

TABLE II

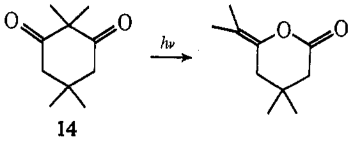
IRRADIATIONS OF THE TRISPIROCYCLOHEXANE-1,3,5-TRIONES

5, *n*	Solvent (*M*)	Time, hr	Products (% yield)
4	Pentane (0.016)^{a}	1	**5**, *n* = 4 (4), **6** (30), **7** (11.4)^{b}
5	Pentane (0.015)^{c}	80	**4**, *n* = 5 (14.1)^{d}
5	Pentane (0.014)^{c}	65	**4**, *n* = 5 (1),^{e} **8**(7),^{f} **9** (8)^{g}
5	Pentane (0.01)^{a}	3	**4**, *n* = 5 (10.0)^{e}
5	Acetone (0.01)^{h}	12.5	**8** (33)^{f}
6	Pentane (0.015)^{a}	89.5	**4**, *n* = 6 (1),^{e} **10** (15.2),^{i} **11** (3.2),^{j} **12** (1.2)^{g}
6	Pentane (0.03)^{a}	90.5	**4**, *n* = 6 (4.2)^{e}
6	Pentane (0.002)^{h}	12	**10** (51)^{k}
6	Acetone (0.002)^{h}	12	**10** (66)^{k}
7	Pentane (0.022)^{a}	6	**4**, *n* = 7 (1.6),^{e} **13** (19)^{f}

^{a} Corex filter. ^{b} Products isolated by vpc separation. ^{c} Rayonet RPR-100 chamber reactor with 16 253.7-nm lamps. ^{d} Eluted with hexane on neutral alumina followed by passing through a silver nitrate impregnated alumina column followed by vpc purification on a silicone column (160°). ^{e} Eluted with hexane and purified on a silver nitrate impregnated alumina column. ^{f} Eluted with a 1:1 hexane–benzene mixture. ^{g} Eluted with ether. ^{h} Pyrex optics. ^{i} Eluted with 4:1 hexane–benzene. ^{j} Eluted with benzene. ^{k} Crude reaction mixture crystallized from ether.

diradical. The observation that no isomeric δ lactone in the photolysis of trione **5** (*n* = 6) was seen could be due to the long irradiation times and possible destruction under the photochemical conditions employed. The δ lactone isomeric with trione **5** (*n* = 4) is unstable to ultraviolet irradiation.

Other diradical type mechanisms have been proposed in analogous reactions. Nozaki and coworkers[20] have reported the isolation of an exocyclic enol δ lactone as the major component in the photolysis of 2,2,5,5-tetramethyl-1,3-cyclohexanedione (**14**). The exocyclic enol lactone arises *via* a mesomeric C,O diradical. Also, Hostettler[8] has rationalized the formation of 4-hydroxy-2,2,3,3,5-pentamethyl-4-hexenoic acid λ-lactone (**15**) and 2,2,3,3-tetramethyl-4-isopropylideneoxetane (**16**) from hexamethylcyclopentane-1,3-dione and hexamethylcyclobutanone, respectively, *via* mesomeric C,O diradicals formed from the initial C,C diradical.



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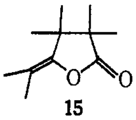

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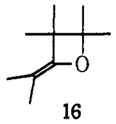

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TABLE III

PHYSICAL PROPERTIES AND SPECTRAL DATA FOR THE PHOTOLYSIS PRODUCTS

Structure	Mp, °C	Ir (CCl_4), cm^{-1}	Nmr ($CDCl_3$), δ
4, *n* = 5^{a}	34–35	2955, 2865, 1455	1.13–1.87 (m)
4, *n* = 6^{b}	119–120	2980, 2925, 1445	1.47 (broad s)
4, *n* = 7^{c}	61–63	2910, 2855, 1460	1.57 (broad s)
6^{d}	*e*	1715, 1765	2.85–3.23 (4 H, m)
			1.78–2.85 (12 H, m)
7^{f}	*e*	1715, 1755	2.19–2.44 (6 H, m)
			1.59–2.19 (12 H, m)
8^{g}	62–64	1715, 1750	1.85 (broad s)
			1.67 (broad envelope)
9^{h}	44–45	1755	1.70 (broad s)
			1.64 (broad s)
10^{i}	93–94	1705, 1745	1.61 (broad)
11^{j}	150–151	1680, 1780	2.30 (4 H, broad envelope)
			1.60 (26 H, broad envelope)
12^{k}	126–128	1750	1.60 (broad envelope)
13^{l}	103–105	1715, 1750	1.63 (broad envelope)

^{a} *Anal.* Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 12.00. ^{b} *Anal.* Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.80; H, 12.05. ^{c} *Anal.* Calcd for $C_{21}H_{36}$: C, 87.42; H, 12.58. Found: C, 87.13; H, 12.42. ^{d} *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 72.99; H, 7.27. ^{e} Isolated by vpc collection from a Silicone GE-SS-96 on Firebrick column. ^{f} *Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.03; H, 8.58. ^{g} *Anal.* Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.49; H, 9.43. ^{h} *Anal.* Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.67; H, 10.31. ^{i} *Anal.* Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.06; H, 9.68. ^{j} *Anal.* Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.62; H, 9.89. ^{k} Insufficient material for analysis. ^{l} *Anal.* Calcd for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.22; H, 10.80.

The multiplicity of the excited state involved in the transformation of trione **5** (*n* = 6) to hydrocarbon **4** (*n* = 6) apparently cannot be established by the preparative experiments reported here. It might be noted that benzophenone did not sensitize the monodecarbonylation of hexamethylcyclohexane-1,3,5-trione, and it has been suggested that this photoreaction occurs from the n–π* singlet.[8] Photolysis of this trione in acetone as solvent (and presumably sensitizer) led mainly to unchanged trione. Trimers **5** (*n* = 5 or 6) on irradiation in acetone solution led to **8** (32.6%) and **10** (66%), respectively. The photolysis of dione **10** in acetone solution led to a poor yield of **4** (*n* = 6) (1%). The acetone sensitizations are suggestive of a n–π* triplet as the chemically reactive species in the latter three cases.[21]

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 237-B grating infrared spectrophotometer. Ultraviolet spectra above 215 nm

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(20) H. Nozaki, Z. Yamaguti, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, **23**, 3993 (1967).

(21) The multiplicity of the excited state(s) has (have) certainly not been clearly established. See J. M. Beard and R. H. Eastman, *Tetrahedron Lett.*, 3029 (1970), and N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971), and references cited therein.

were taken using a Perkin-Elmer 202 ultraviolet–visible spectrophotometer. Nmr spectra were obtained on a Varian Associates A-60 spectrophotometer, and are reported as parts per million relative to internal TMS. Mass spectra were taken on a JMS-01SG Mattauck-Herzog type double focusing mass spectrometer by Jeolco, Inc., Medford, Mass. Gas chromatography was performed on an Aerograph Model A-90-P instrument. Microanalyses were done by Robertson Laboratory, Florham Park, N. J.

Materials.—Pentane (Eastman Organic Chemicals), purified by oleum and permanganate, was used as received. Acetone (Fisher Scientific, Certified A. C. S.) was used as received. *n*-Hexane used for column chromatography was purified by shaking with concentrated sulfuric acid, washing with water, drying with calcium chloride, and distilling from phosphorus pentoxide. Benzene used for column chromatography was distilled from sodium. Silver nitrate–alumina was prepared by the procedure of Murray and coworkers.[22]

Hexasubstituted Cyclohexane-1,3,5-triones.—Hexamethylcyclohexane-1,3,5-trione was prepared by the procedure described by Erickson and Kitchens.[23] This trione exhibited infrared absorption (CCl_4) at 1698 cm^{-1}, exhibited a singlet at δ 1.38 ppm ($CDCl_3$) in the nmr, and showed uv absorption maxima (CH_3OH) at 226 (ϵ 340) and 297 nm (ϵ 85). The properties and spectral data for the trispirocyclohexane-1,3,5-triones **5** (n = 4, 5, 6, or 7) are tabulated in Table I.

General Irradiation Procedure.—The solvent employed was degassed by slowly bubbling nitrogen through the solution for 5 min. A degassed solution of the compound in pentane or acetone (generally 1.7–2.7 mmol of compound in 170 ml of solvent) was irradiated with a 450-W Hanovia mercury-vapor lamp, No. 6-79A-36, in a quartz immersion well apparatus fitted with a Pyrex or Corex filter. The reaction progress was monitored periodically by infrared analysis. Upon termination of the irradiation, the solution was filtered in those cases where insoluble material formed. The solution was concentrated and the residue was subjected to purification by column chromatography on neutral alumina or vpc separation or the residual material was crystallized.

Typical Irradiation. Photolysis of Hexamethylcyclohexane-1,3,5-trione.—A degassed solution of 422 mg (2.0 mmol) of the trione in 170 ml of pentane was irradiated using a Pyrex filter for 4 hr. After removal of the solvent, hexamethylcyclopentane-1,3-dione was isolated by vpc (6 ft 20% GE-SS-96 on Firebrick; column operated at 196° with an He flow rate of 75 ml/min). There was obtained 174.3 mg (48.0%) of the dione, mp 49.5–51.5° (lit.[8] mp 51°).

A degassed solution of 535 mg (2.54 mmol) of hexamethylcyclohexane-1,3,5-trione in 700 ml of acetone was irradiated for 4 hr using a Pyrex filter. After removal of the acetone, crystallization from ether yielded 349 mg (65.4%) of starting trione.

The pertinent experimental conditions and results for the irradiations of the trispirocyclohexane-1,3,5-triones are summarized in Table II.

Irradiation of 10.—A degassed solution of **10** (468 mg, 1.55 mmol) in 170 ml of acetone was irradiated for 73 hr using Pyrex optics. After solvent removal, the residue was dissolved in hexane and chromatographed on neutral alumina. A hydrocarbon fraction was collected which was rechromatographed on a silver nitrate impregnated alumina column to yield 2.3 mg (1%) of **4** (n = 6). Elution with ether yielded starting material (30% recovery).

The physical properties and the spectral data for the photolysis products are tabulated in Table III.

Base-Catalyzed Thermal Rearrangement of 6 to 5 (n = 4).—A solution of 135 mg (0.55 mmol) of **6** in 2.0 ml of dry benzene was heated to reflux. Upon adding 40 mg of $NaOCH_3$ an exothermic reaction occurred. Following 15 min of additional heating, the orange-colored solution was cooled and neutralized with a few drops of glacial acetic acid. The mixture was extracted with ether and the organic phase was dried over K_2CO_3. After solvent removal, 80.0 mg (59.2%) of an oil was obtained. Vpc analysis (6 ft 20% Silicone GE-SS-96 on Firebrick, column operated at 185°) yielded 34.5 mg of a component that had ir and vpc retention time identical with those of **5** (n = 4).

Registry No.—**4** (n = 5), 29150-89-8; **4** (n = 6), 33780-60-8; **4** (n = 7), 33777-05-8; **6**, 33777-06-9; **7**, 33777-07-0; **8**, 29798-98-9; **9**, 29798-99-0; **10**, 33777-10-5; **11**, 33777-11-6; **12**, 33777-12-7; **13**, 33777-13-8.

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A Model Iron-Catalyzed Biomimetic Cyclization of a Cyclic Tryptamine *N*-Oxide

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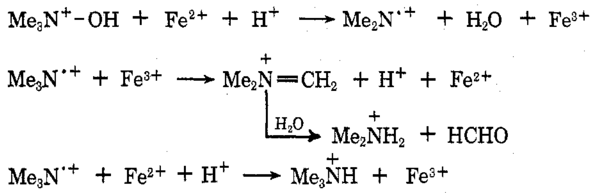
The tryptamine *N*-oxide **5** is cleanly converted to the tetracyclic amine **6** with hydrated ferrous sulfate in methanolic acetic acid. The biosynthetic significance, synthetic potential, and mechanistic implications of the reaction are considered.

The iminium ion **1**, derived from stemmadenine,[2] appears to be a key intermediate in the biogenetic relationship between preakuammicine **2** and precondylocarpine **3**, and thus occupies a central position in the later stages of indole alkaloid biogenesis. The elegant cyclization reactions of Kutney,[3] Schmid,[4] and their coworkers clearly illustrate the potential of synthetically generated iminium ions for realizing analogous conversions. We now report that an iminium species, generated under very mild conditions from an *N*-oxide function, can undergo clean internal cyclization to give a β-carboline which may serve as a model in indole alkaloid biogenesis; in addition, we record some findings which relate to the mechanisms of analogous reactions *in vitro* and *in vivo*.

The dealkylation of tertiary amine oxides with aqueous Fe^{2+} has been extensively investigated, and the following mechanism has been proposed[5] for trimethylamine *N*-oxide.



$$Me_3N^{+}\text{-}OH + Fe^{2+} + H^{+} \longrightarrow Me_2N^{\cdot +} + H_2O + Fe^{3+}$$

$$Me_3N^{\cdot +} + Fe^{3+} \longrightarrow Me_2\overset{+}{N}{=}CH_2 + H^{+} + Fe^{2+} \xrightarrow{H_2O} Me_2\overset{+}{N}H_2 + HCHO$$

$$Me_3N^{\cdot +} + Fe^{2+} + H^{+} \longrightarrow Me_3\overset{+}{N}H + Fe^{3+}$$

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[1] To whom inquiries should be addressed.

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