

methylene shifts closely parallel those observed for the cyclophane lacking the hydroxyl group.<sup>1</sup>

**4,4'-Dihydroxy[10,10]metacyclophane (12, n = 2):**  $\delta$  6.57 (s, H-4), 6.47 (s, H-2), 4.77 (s, OH), 2.51 (t,  $J = 7.5$  Hz,  $\alpha$ -CH<sub>2</sub>), 1.57 (m,  $J = 7.5$  Hz,  $\beta$ -CH<sub>2</sub>), 1.25 (br s, other CH<sub>2</sub>'s).

**1,10-Bis(3-hydroxy-5-methylphenyl)decane (13, m = 10, n = 1):**  $\delta$  6.57 (s, H-2,4), 6.47 (s, H-6), 4.78 (s, OH), 2.50 (t,  $J = 7.3$  Hz,  $\alpha$ -CH<sub>2</sub>), 2.27 (s, Me), 1.57 (m,  $J = 7.3$ ,  $\beta$ -CH<sub>2</sub>), 1.27 (br s, other CH<sub>2</sub>'s).

**Oxidation of Trianion 3,5-4 with Cuprous Bromide.** Anhydrous cuprous bromide (5.74 g, 20 mmol) was added to a suspension of trianion 3,5-4 in THF, giving a black color. After the mixture was stirred 18 h, water (20 mL) was added, giving a green color which changed to violet on acidification with 5 N HCl. Workup as above gave **13** ( $m = 2, n = 1$ ) (40%) and **13** ( $m = 2, n = 2$ ) (35%).

**1,2-Bis(3-hydroxy-5-methylphenyl)ethane (13, m = 2, n = 1):**  $\delta$  6.61 (s, H-4), 6.50 (br s, H-2,6), 4.63 (s, OH), 2.80 (s, CH<sub>2</sub>), 2.29 (s, Me).

**3,5-Bis(2-(3-hydroxy-5-methylphenyl)ethyl)phenol (13, m = 2, n = 2):**  $\delta$  (acetone-d<sub>6</sub>) 8.15 (s, central OH), 8.13 (s, other OH's), 6.58 (s, central H), 6.55 (s, H-6), 6.53 (s, H-2,4), 6.49 (s, other H's on central ring), 2.74 (s, CH<sub>2</sub>), 2.21 (s, Me).

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### Short-Lived Intermediates. 9. Polar Alkene Photochemistry and the Perpendicular Alkene Question<sup>1</sup>

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The synthesis of alkenes with twisted double bonds has attracted much attention<sup>2</sup> particularly since the isolation of stable Bredt's rule violators.<sup>3</sup> All known examples have introduced twist by locating the double bond in a ring, e.g. **1**,<sup>4</sup> or attaching bulky substituents, e.g. **2**.<sup>5</sup> Ab initio calculations have shown that 90°-twisted double bonds might be stabilized by suitable selection of substituents, e.g. **3**.<sup>6a</sup> This prediction has never been experimentally addressed.<sup>6,7</sup>

(1) For previous articles in this series, see: Gano, J. E.; Chien, D. H.-T. *J. Am. Chem. Soc.* **1980**, *102*, 3182.

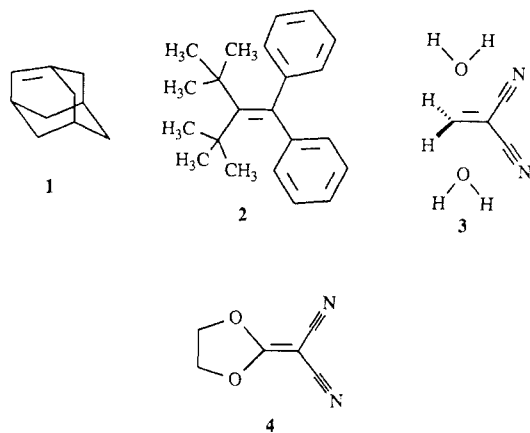
(2) (a) Liebmann, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Keese, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528.

(3) (a) Wiseman, J. A.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956. (b) Marshall, J. A.; Faubl, A. *J. Am. Chem. Soc.* **1970**, *92*, 948.

(4) (a) Conlin, R. T.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1979**, *101*, 7637. (b) Martella, D. J.; Jones, M., Jr.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 2896. (c) Burns, W.; Grant, D.; McKervey, M. A.; Step, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 234. (d) Burns, W.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1974**, 858. (e) Alberts, A. H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1973**, *14*, 3047; (f) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973**, *95*, 972; (g) Lenoir, D. *Tetrahedron Lett.* **1972**, *13*, 4049. (h) Lenoir, D.; Firi, J. *Justus Liebigs Ann. Chem.* **1974**, 1467. (i) Grant, D.; McKervey, M. A.; Rooney, J. J.; Samman, N. G.; Step, G. *J. Chem. Soc., Chem. Commun.* **1972**, 1186.

(5) Mugnoli, A.; Simonetta, M. *J. Chem. Soc. Perkin Trans. 2* **1976**, 1831.

(6) (a) Salem, L.; Stohrer, R. *J. Chem. Soc., Chem. Commun.* **1975**, 140. (b) Salem, L. *Isr. J. Chem.* **1975**, *14*, 89. (c) Bonacic-Koutecky, V.; Bruckmann, P.; Hiberty, P.; Koutecky, J.; Leforestier, C.; Salem, L. *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 575. (d) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41. (e) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (f) Salem, L.; Dauben, W. G.; Turro, N. J. *J. Chem. Phys.* **1973**, *70*, 694. (g) Nagase, S.; Morokuma, K. *J. Am. Chem. Soc.* **1978**, *100*, 1661. (h) Bruni, M. C.; Daudey, J. P.; Langlet, J.; Malrieu, Y. P.; Momicchioli, F. *J. Am. Chem. Soc.* **1977**, *99*, 3487. (i) Apeloig, Y.; Schleyer, P. v. R.; Binkley, J. S.; Pople, S. A. *J. Am. Chem. Soc.* **1976**, *98*, 4332. (j) Devaquet, A. *Pure Appl. Chem.* **1975**, *41*, 455.



In our continuing pursuit of highly twisted alkenes, the photochemistry of 2-(dicyanomethylene)-1,3-dioxacyclopentane (**4**), a push-pull substituted alkene, was undertaken to test the ab initio prediction and to initiate a study of the photochemistry of push-pull substituted alkenes.<sup>8</sup> Thermal equilibration of the singlet excited state of **4** in a polar environment, on the basis of Salem's report,<sup>6a</sup> was expected to lead to a twisted geometry, twist angle  $\sim 75^\circ$ . That twisted excited state was expected to drop to the ground state energy surface onto an energy maximum on opposite sides of which were the planar ground state and the 90°-twisted ground-state conformations. Some of the relaxing hot molecules were expected to partition into the 90°-twisted conformation, which would be stable at 10 K.

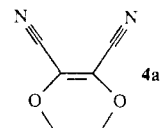
Push-pull substituted alkene **4** was readily prepared<sup>9</sup> and deposited, via vacuum sublimation, or codeposited with diluents onto a cryostat window at low temperatures (10–20 K). Extra care was necessary to insure that highly polar **4** was not associated in the matrices.<sup>10</sup> Although stable to 300-nm light, **4** readily reacted, giving similar results, when exposed to 254-nm (mercury) or 229-nm (cadmium) light.

Irradiation (229 nm) of **4**, matrix-isolated in argon, produced species with IR absorptions at 2172 (m), 1727 (w), 1601 (s), 1452 (w), and 1155 (m, sh)  $\text{cm}^{-1}$  (Figure 1). The UV spectrum showed a new, broad absorption ( $\sim 265$  nm) red-shifted from the absorption of **4** at 232 nm (isospeptic point 254 nm). Simultaneous IR/UV monitoring linked all new bands to the same primary products. Warming for  $1/2$  h (35 K) had no significant effect on the

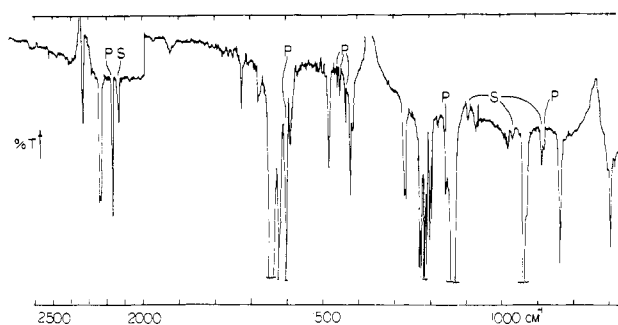
(7) A related question, "sudden polarization," has received limited but significant attention. See: (a) Bonneau, R.; Jousot-Dubien, J.; Yarwood, J.; Pereyre, J. *Tetrahedron Lett.* **1977**, 235. (b) Bonneau, R.; Fournier de Violet, P.; Jousot-Dubien, J. *Nouv. J. Chim.* **1977**, *1*, 31. (c) Bonneau, R.; Fournier de Violet, P. *C. R. Seances Acad. Sci., Ser. C* **1977**, *284*, 631.

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(9) Contrary to the literature report that **4** was an unstable, pink solid, mp 115–116.5 °C, vacuum sublimation gave a colorless solid, mp 119–120 °C. See: (a) Dickson, C. L.; Melby, L. R. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 276. (b) Careful inspection of the literature revealed the reported structural assignment for **4** to be ambiguous since the mechanistically less likely but accessible isomer **4a** was not ruled out. Since **4** was found to show four signals in its <sup>13</sup>C NMR spectrum, this uncertainty was removed.

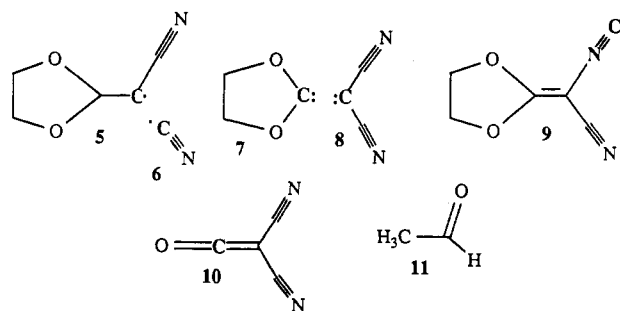


(10) Aggregation of this very polar alkene was clearly evident in the heptane matrix by the appearance of a new C=C stretching band at 1615  $\text{cm}^{-1}$  at the expense of the sharp monomer band at 1635  $\text{cm}^{-1}$  when the matrix was heated to 35 K.



**Figure 1.** Infrared spectrum of photolyzed (229 nm) **4**, matrix-isolated in argon at 10 K, recorded at  $\sim \times 3$  ordinate scale expansion. The sample was deposited and photolyzed on both sides of the cesium iodide window. (P) Primary photoproducts, (S) secondary photoproducts. Unmarked absorptions are mostly residual **4**.

spectra. Even with a layer-photolysis-layer (44 cycles) sequence, it was not possible to convert most of **4** to new materials before significant secondary photochemistry became evident.



A variety of species, e.g. **5**–**11**, could account for the absorptions. Radicals, **5** and **6**, and carbenes, **7** and **8**, would not be expected to persist upon warming to 35 K. Also, the known IR absorption bands for **8**<sup>11</sup> were absent. The necessary isonitrile bands, 2130 and 1645  $\text{cm}^{-1}$ , from **9** were absent.<sup>12</sup> Development of a new synthesis of here-to-fore unknown **10** revealed that it possessed an intense "ketene" absorption band exactly matching the primary photoproduct 2172- $\text{cm}^{-1}$  band.<sup>13,14</sup> Likewise, the carbonyl absorption of acetaldehyde, **11**, matched the 1727- $\text{cm}^{-1}$  primary product band. Other less intense bands from **10** and **11** were not likely to be observed because the conversion to primary products was not great; *vida supra*. These observations, and others made below, strongly support **10** and **11** as the primary photoproducts in this system. The photochemical expulsion of a ketene in a system like **4** is without precedent.<sup>15,16</sup> However, ethers show photochemical C–O bond cleavage, e.g. **12**  $\rightarrow$  **13**, **14**

(11) Smith, W. H.; Leroi, G. E. *Spectrochim. Acta Part A* 1969, 25, 1917.

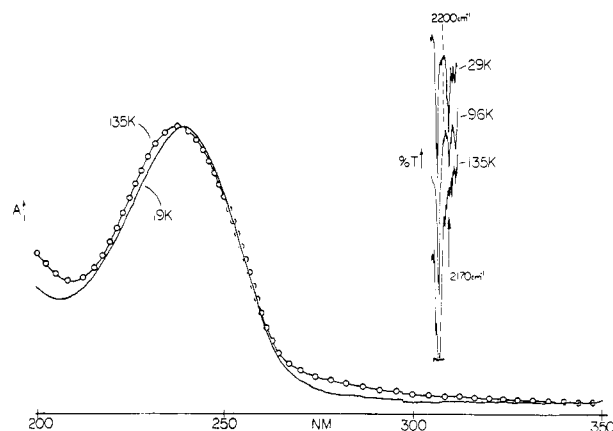
(12) Upon going from **4** to **9**, the frequency shifts would be expected to parallel those observed between vinyl cyanide and vinyl isocyanide,  $\Delta\nu^{\text{CN}} = -110 \text{ cm}^{-1}$ ,  $\Delta\nu^{\text{CC}} = 0$ . See: Matteson, D. S.; Bailey, R. A. *J. Am. Chem. Soc.* 1968, 90, 3761.

(13) (a) Neidlein, R.; Bernhardt, E. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 369. (b) Hetzel, A.; Neidlein, R.; Schulz, R.; Schweig, A. *Ibid.* 1980, 19, 739.

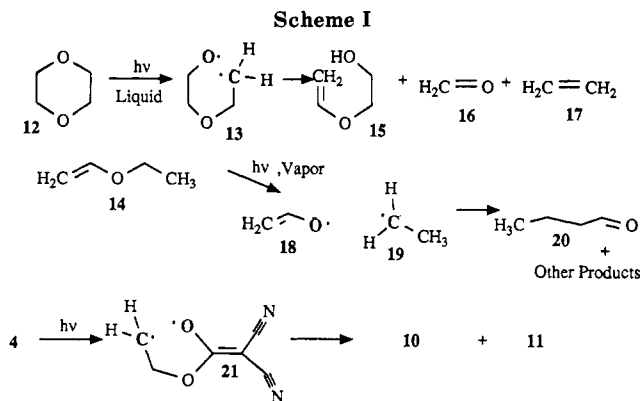
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**Figure 2.** Ultraviolet absorption spectrum after **4**, matrix isolated in heptane at 19 K, was 34% photocomposed (—) and after subsequently warming to 135 K (○). Infrared spectrum showing 2200- $\text{cm}^{-1}$  region after **4**, matrix isolated in heptane at 19 K, was partially photodecomposed and then gradually warmed to 29, 96, and 135 K. Note the gradual disappearance of the band at  $\sim 2170 \text{ cm}^{-1}$ .



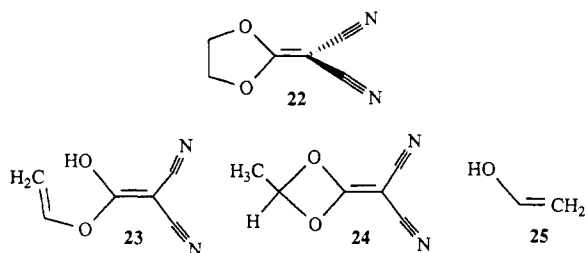
$\rightarrow$  **18** + **19**.<sup>17a-c</sup> Thus, a reasonable path to **10** and **11** is shown in Scheme I.

Having identified the species responsible for the other IR bands, only the 1601- $\text{cm}^{-1}$  IR band and the UV absorptions could possibly be assigned to the perpendicular alkene being sought. Since the IR spectrum of twisted **4** should be similar to that of **4** itself and the C=C stretching absorption should be somewhat lower than in **4**, the 1601- $\text{cm}^{-1}$  band could have been the twisted conformer. CNDO/S calculations suggested this conformer would show extremely weak  $^1A_2$  and  $^1B_1$  transitions at 1016 and 331 nm, respectively, and a somewhat stronger  $^1B_2$  transition at 288 nm. For comparison, the same calculations predicted the absorption of **4** observed at 232 nm (argon) to be a  $^1B_1$  transition at 269 nm.

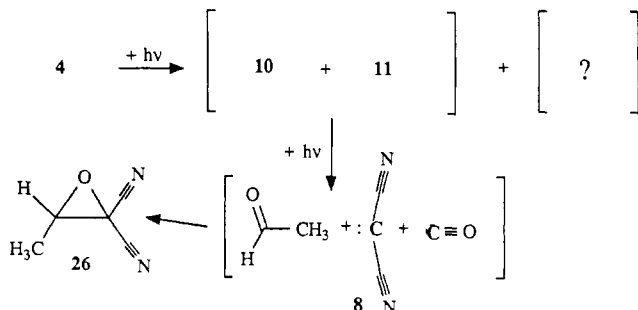
The fact that perpendicular alkene **22** was expected to readily revert back to planar **4** upon warming<sup>6a</sup> suggested additional experiments, wherein the new species were heated, would be useful. Alkene **4** was irradiated while matrix isolated in heptane,<sup>10</sup> water (a polar matrix), and acetonitrile (a polar matrix) and as a neat solid. In heptane, the 1601- $\text{cm}^{-1}$  band was obscured. However, the 2172- $\text{cm}^{-1}$  band disappeared as the temperature approached 100 K, which was consistent with the high reactivity of **10**. In all cases, however, the UV spectra, e.g. Figure 2, demonstrated the disappearance of **4** upon irradiation but no reappearance of **4** as the temperature

(17) (a) Von Sonntag, C.; Schuchmann, H. P. *Adv. Photochem.* 1972, 10, 59. (b) Marad, E. *J. Am. Chem. Soc.* 1961, 83, 1327. (c) Morris, R. V.; Filseth, S. V. *Can. J. Chem.* 1970, 48, 924.

was raised. Quite clearly, no perpendicular alkene was formed, even in polar media, from this particular push-pull substituted alkene. Other possible species which might account for the 1601-cm<sup>-1</sup> band are 23-25.



Extended irradiation of 4 in argon demonstrated that secondary photoproducts were responsible for the IR bands at 2140, 1080, 970, and 890 cm<sup>-1</sup> (Figure 1) along with additional bands, which eventually became visible, at 2250 (w), 2230 (m), 2200 (w), 1280 (w), 1200 (m), 1125 (w), 1115 (w), 1090 (m), 970 (m), and 890 (s) cm<sup>-1</sup>. Chemical deduction suggested the final photostable products to be carbon monoxide and 2,2-dicyano-3-methyloxirane (26). Confirmation was made by comparison of the IR spectrum (argon) of an authentic sample, prepared by the epoxidation of the appropriate alkene, with the observed bands. In addition, the NMR bands for 26 were evident in the spectrum of a sample collected from the cesium iodide window after photolysis of 4. These new products



were readily rationalized by the addition of carbene 8,<sup>11</sup> formed photochemically from 10, to the C=O bond of the acetaldehyde trapped adjacent to 8 in the matrix. This unique addition reaction suggested this route might be useful for further studies of the addition of carbenes to carbonyl compounds.

In conclusion, the data rule out a significant buildup of a perpendicular alkene during the low-temperature photolysis of 4. As such, this argues against the existence of such intermediates in general. The first detailed photochemical study of a dipolar alkene in an apolar environment was shown to provide a novel fragmentation to dicyanoketene and acetaldehyde. In polar solution, no reaction occurred at room temperature. The photochemistry of caged dicyanoketene/acetaldehyde lead to a unique, direct insertion of dicyanocarbene into a C=O bond.

### Experimental Section

Matrix isolation was performed on an Air Products CS-202 cryostat temperature controlled with the APD IC-2 controller. Perkin-Elmer 621 and Beckman Acta III spectrophotometers respectively were used to produce IR and UV spectra. Abraded potassium bromide or quartz disks in the reference beam compensated for light scattering. Matrix materials were argon (ultrahigh purity), heptane (concentrated H<sub>2</sub>SO<sub>4</sub>, distilled), acetonitrile (Spectral Grade), and water (triply distilled). Photochemical light sources were the unfiltered emission from Pen-Ray low-pressure mercury (254 nm) or Phillips low-pressure cadmium (229 nm) resonance lamps.

**2-(Dicyanomethylene)-1,3-dioxacyclopentane (4)** was prepared by a reported method.<sup>9a</sup> Vacuum (0.1 mm) sublimation of the crude, pink product proceeded readily at 5–10 °C below the melting point, giving colorless crystals of 4: mp 119–120.5 °C; NMR (CDCl<sub>3</sub>) δ 4.88 (s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, CD<sub>3</sub>CN) 40.22, 71.45 (CH<sub>2</sub>), 11.96 (CN), 178.36 (=C(OR)<sub>2</sub>); IR (CHCl<sub>3</sub>), 2225 (CN), 1613 (C=C), 1140 cm<sup>-1</sup>; UV<sub>max</sub> (CH<sub>3</sub>CN) 239 nm (ε 24000).

**2,2-Dicyano-3-methyloxirane (26).** 1,2-Dichloroethane (8.5 g), 1,1-dicyanopropene (0.10 g, 1.1 mmol), *m*-chloroperbenzoic acid (0.28 g, 1.6 mmol), and a little 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide were heated at (50–90 °C) for 26 h. The supernatant liquid was decanted after the volume was reduced (vacuum) to 4 mL and again after it was reduced to 1 mL. The resulting liquid was fractionated by GC (20% Apiezon L, 140 °C) to give 1,2-dichloroethane, a little 1,1-dicyanopropene, and predominantly, moderately stable 26: NMR (CDCl<sub>3</sub>) δ 1.66 (d, *J* = 5 Hz), 3.77 (q, *J* = 5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.7, 39.3, 62.4, 110.7, 111.7; IR (CCl<sub>4</sub>) 2250, 1430, 1400, 1275, 1195, 1130, 1105, 990, 880, 875 cm<sup>-1</sup>.

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**Registry No.** 4, 5694-65-5; 8, 1884-65-7; 9, 109960-67-0; 10, 4361-47-1; 11, 75-07-0; 26, 109960-66-9; 1,1-dicyanopropene, 1508-07-2.

### Indole as a Dienophile in Inverse Electron Demand Diels-Alder Reactions. 5*H*-Pyridazino[4,5-*b*]indoles as Cycloadducts with 3,6-Dicarbomethoxy-1,2,4,5-tetrazine

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The indole skeleton is a fundamental structural unit of numerous biologically active alkaloids. As such, the chemistry of indole has been widely investigated<sup>1</sup> and the indole-based alkaloids have been the target of countless synthetic efforts. Indole could prove to be an appropriate starting material for further alkaloid syntheses if suitable chemistry can be coaxed from this parent skeleton. The recent applications by Boger<sup>2</sup> and others<sup>3</sup> of the inverse electron demand Diels-Alder cycloaddition<sup>4</sup> in organic synthesis has turned our interest to the possibility of using indole as a dienophile for constructing higher alkaloids.

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