

## Photochemical Functionalization of Cubanes

A. Bashir-Hashemi\* and Jianchang Li

GEO-CENTERS, INC., at ARDEC, 762 Route 15 South, Lake Hopatcong, New Jersey 07849

Nathan Gelber

Armaments Research, Development &amp; Engineering Center, Picatinny Arsenal, New Jersey 07806

Herman Ammon

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received August 30, 1994<sup>⊗</sup>

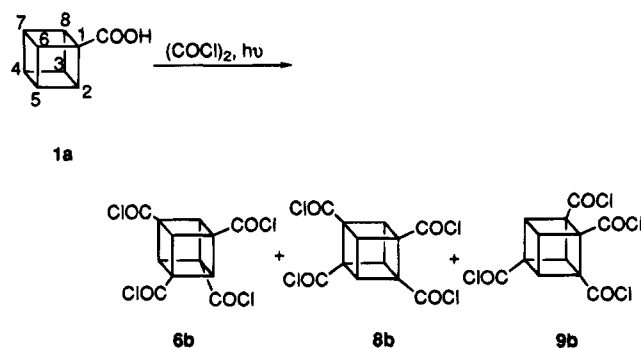
A wide range of cubanecarboxylic acids has been prepared by a simple and efficient photochemical process. Chlorocarbonylation of cubanecarboxylic acid with oxalyl chloride under UV irradiation produced polysubstituted cubanes with chlorocarbonyl groups predominantly on the remote sites ( $\beta$  or  $\gamma$ ). The  $T_d$ -tetraacid chloride **6b**, in which chlorocarbonyl groups are in alternate positions, was the major product. Irradiation of 1,2,3,7-tetrasubstituted cubane **9** with oxalyl chloride gave pentasubstituted cubane **10**. Other isomers, 1,3,5,7-tetrasubstituted cubane **6** and 1,2,4,7-tetrasubstituted cubane **8**, in which chlorocarbonylation would occur at positions ortho to three or two carbonyl groups, gave only chlorinated products. Photochemical reaction of oxalyl chloride with nitrocubanes gave chlorocarbonylated and chlorinated nitrocubanes. *Ab initio* calculations show carbon-hydrogen bond strength at different positions of the cubane is not the major factor in determining the regioselectivity of the chlorocarbonylation. A polar effect might be the key factor in site selectivity.

Cubane and its derivatives belong to the class of strained cage compounds which have been at the forefront in the search for new high energy materials over the past decade.<sup>1</sup> The rigid framework of the cubane molecule, in which multiple functional groups would possess unique arrangements, also shows potential application for use in pharmaceutical and polymer chemistry.<sup>2</sup> Areas of the most recent interest are dendrimers and combinatorial chemistry.<sup>3</sup>

The multifunctionalization of the cubane skeleton has been a challenging task for organic chemists. Anionic reactions<sup>4</sup> as well as radical and cationic reactions have been used for synthesis of substituted cubanes although the cubyl radical<sup>5</sup> and cation<sup>6</sup> have unfavorable, nonplanar geometries. A large number of cubanecarboxylic acids have been prepared using ortho-directed metalation.<sup>4</sup> However, the lengthy synthetic sequences required

for the preparation of some of these materials have limited their practical application.

We have recently reported an efficient photochemical chlorocarbonylation of a series of cyclic and acyclic carbonyl compounds with oxalyl chloride.<sup>7</sup> Many carboxycubanes have now been synthesized by employing this photochemical process.<sup>8</sup> For example, tetrasubstituted cubanes **6b**, **8b**, and **9b** can be obtained easily in a single step from carboxycubane **1a**. In this methodology



<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, January 1, 1995.  
(1) *Chemistry of Energetic Materials*; Olah, G. A., Squire, D. R., Eds.; Academic Press: San Diego, CA, 1991.

(2) Eaton, P. E. *Angew. Chem.* **1992**, *104*, 1447. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1421. Higuchi, H.; Ueda, I. in *Carbocyclic Cage Compounds; Chemistry and Applications*; Osawa, E. J., Yonemitsu, O., Eds.; VCH: New York, 1992; pp 217-244.

(3) Carell, T.; Wintner, E. A.; Bashir-Hashemi, A.; Rebek, J., Jr. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2059.

(4) Bashir-Hashemi, A. *J. Am. Chem. Soc.* **1988**, *110*, 7234. Eaton, P. E.; Lee, C.-H.; Xiong, Y. *Ibid.* **1989**, *111*, 8016. Bashir-Hashemi, A.; Ammon, H. L.; Choi, C. S. *J. Org. Chem.* **1990**, *55*, 416. Bottaro, J. C.; Pennwell, P. E.; Schmitt, R. J. *Ibid.* **1991**, *56*, 1306. Castaldi, G.; Colombo, R.; Allegrini, P. *Tetrahedron Lett.* **1991**, *32*, 2173. Eaton, P. E.; Xiong, Y.; Zhou, J. P. *J. Org. Chem.* **1992**, *57*, 4277.

(5) Eaton, P. E.; Xiong, Y.; Yang, C.-X. *J. Am. Chem. Soc.* **1990**, *112*, 3225. Hrovat, D. A.; Borden, W. T. *Ibid.* **1990**, *112*, 3227. Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. L. *Ibid.* **1990**, *112*, 3228. Olah, G. A.; Lee, C. S.; Parakash, G. K. S.; Moriarty, R. M.; Rao, M. S. C. *J. Am. Chem. Soc.* **1993**, *115*, 10728.

(6) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271. Della, E. W.; Elsej, G. M.; Head, N. J.; Walton, J. C. *J. Chem. Soc. Chem. Commun.* **1990**, 1589. Reddy, D. S.; Maggini, M.; Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1991**, *31*, 805. Walton, J. C. *Chem. Soc. Rev.* **1992**, *2* (12), 105. Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.*, **1992**, *114*, 10730. Della, E. W.; Schiesser, C. H. *J. Chem. Soc. Chem. Commun.* **1994**, 417.

electron-withdrawing groups are used to direct substitutions predominantly to positions other than the ortho position. Compound **6b**, in which chlorocarbonylation occurred at the alternate 1, 3, 5, and 7 positions, was the major product in the reaction mixture.

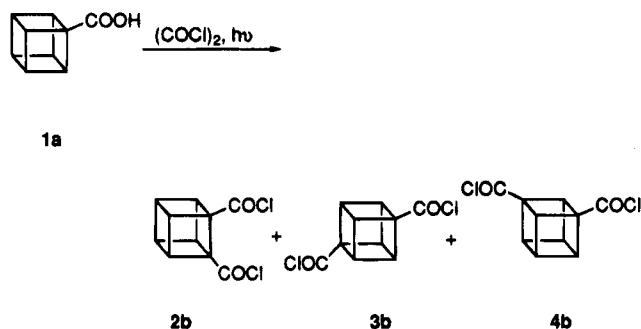
We now report a detailed study of this reaction and its application to the synthesis of other interesting polysubstituted cubanes.

(7) Bashir-Hashemi, A.; Hardee, J. R.; Gelber, N.; Qi, L.; Axenrod, T. *J. Org. Chem.* **1994**, *59*, 2132. Bashir-Hashemi, A.; Li, J.; Gelber, N. *Tetrahedron Lett.* **1995**, in press.

(8) Bashir-Hashemi, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 612. There are 21 cubanecarboxylic acids possible. More than half can be made by this method.

## Results and Discussion

A solution of carboxycubane **1a** and oxalyl chloride was irradiated with a Rayonet photochemical reactor at 35–40 °C and the progress of the reaction monitored by  $^1\text{H}$  NMR. The starting material was consumed after 30 min and 1,2-, 1,4- and 1,3-disubstituted cubanes **2b**, **3b**, and **4b** formed in an approximate ratio of 1:1:3.<sup>9</sup>



The higher concentration of compound **4b** in the reaction mixture can be explained by statistical factors (three ortho, three meta, and one para position) as well as polar effects.<sup>10</sup> The electrophilic chlorocarbonyl or chlorine radicals preferentially abstract a hydrogen from the least electron-deficient carbon atom distant from the electron-withdrawing groups. The importance of steric factors in the substitution pattern can be minimized since the cubane skeleton contains relatively long C–C bonds (1.57 Å) and wide external C–C–H (126°) angles.<sup>2</sup>

*Ab initio* molecular orbital calculations show that functionalization of cubane by an electron-withdrawing group shortens the C–H bonds and presumably makes bond-breaking by a homolytic process more difficult. Thus, cubane should be more reactive and 1,3,5,7-tetranitrocubane less reactive to free radical substitution reactions. *Ab initio* molecular orbital structure optimization and calculations were carried out with the Gaussian 92<sup>11</sup> program system and a 6-31g\* basis set on an IBM RS-6000 workstation Model 370, and the results are given in Table 1.

The changes in the C–H lengths in the monosubstituted cubanes are quite small, but these data do suggest that the reactivity for radical substitution is para > meta > ortho.

Transformation of disubstituted cubanes to tri- and higher substituted cubanes followed (Figure 1). After a reaction period of 8 h, the  $^1\text{H}$  NMR of the product showed spectra consistent with tetrasubstituted cubanes **6b**, **8b**, and **9b** in an approximate 55:10:35 ratio, respectively.

(9) The identity of the reaction products was verified by comparison with authentic samples obtained by other methods. The distribution of products from the first photochlorocarbonylation is highly dependent on temperature, light source, etc. (Eaton, P. E.; Kanomata, N.; Li, J., private communication), but the major ultimate product is the  $T_d$ -tetraacid chloride. We thank Prof. Eaton for informing us of their results.

(10) For factors determining the reactivity and regioselectivity of radical reactions see; Tedder, J. M. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 401. For some interesting papers in the related areas and the importance of polar effects in the transition state see; Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 10730. Hrovat, D. A.; Borden, T. W. *J. Am. Chem. Soc.* **1994**, *116*, 6459.

(11) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

Table 1. C–H Bond Lengths for Four Cubanes from 6-31g\* Geometry Optimizations

compound	bond length (Å)
cubane C–H	1.0810
$\text{NO}_2$ -cubane	
o-C–H	1.0788
m-C–H	1.0794
p-C–H	1.0797
(COCl)-cubane	
o-C–H	1.0794
m-C–H	1.0799
p-C–H	1.0801
1,3,5,7-( $\text{NO}_2$ ) <sub>4</sub> -cubane C–H	1.0760

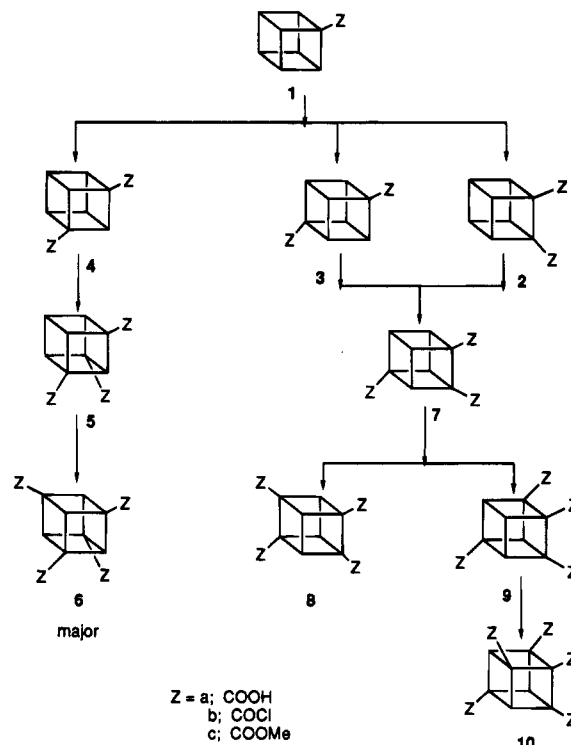


Figure 1.

Compound **6b** was partially separated from other isomers in 40–50% yield by triturating the reaction mixture with ether.

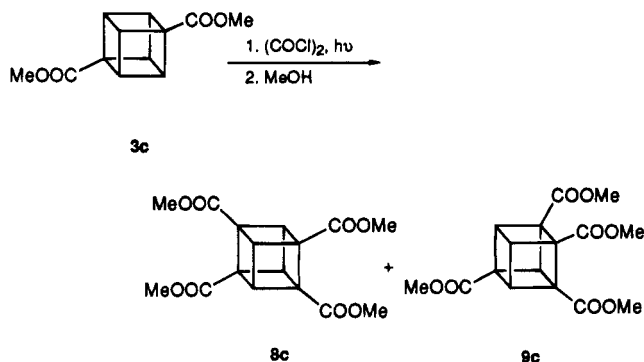
It is noted that the rate of substitution decreases as the reaction progresses. After 18 h of irradiation, pentasubstituted cubane **10b** was obtained with trace amounts of hexa- and heptasubstituted cubanes (as methyl ester, GC-MS). The  $^1\text{H}$  NMR of the pentasubstituted cubane **10b** shows only resonance as a singlet at  $\delta$  5.21 ppm. The origin of  $C_{3v}$  symmetric compound **10b** must be tetrasubstituted cubane **9b**, since that is the only case in which substitution can occur ortho to only one carbonyl group. In compounds **6b** and **8b** C–H bonds are ortho to three and two carbonyl groups, respectively.

When a mixture of tetrakis(chlorocarbonyl)cubanes **6b**, **8b**, and **9b** was subjected to further photochemical chlorocarbonylation, the extent of compound **9b** in the reaction mixture diminished with the formation of compound **10b** while the amounts of the other tetrasubstituted isomers **6b** and **8b** remained unchanged.<sup>12</sup>

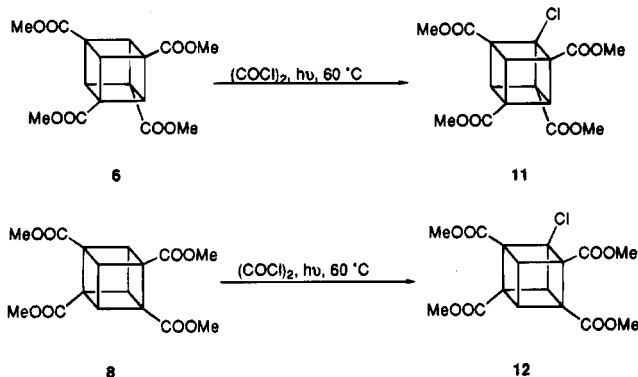
Compounds **8c** and **9c** were obtained in much better yields (60–80% total) from the photochemical reaction

(12) In a separate experiment, compound **10b** was not obtained from **6b** or **8b** under these reaction conditions.  $^1\text{H}$  NMR of pentakis(chlorocarbonyl)cubane obtained from compound **8b** should give multiple resonances.

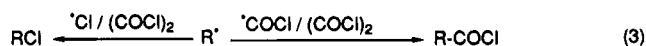
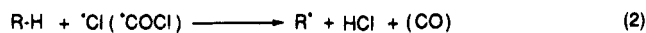
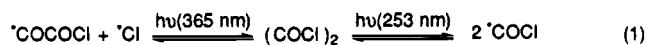
of commercially-available 1,4-dicarbomethoxycubane (**3c**) and oxalyl chloride, followed by esterification with methanol.



The synthesis of more highly substituted cubanes, from compounds **6c** and **8c**, in which the unsubstituted positions are deactivated by the two adjacent carboxyl groups, was achieved under more vigorous reaction conditions. When a solution of these compounds in oxalyl chloride was exposed to photochemical reaction at higher temperatures and prolonged reaction time, only chlorinated products **11** and **12** were obtained.<sup>13</sup>



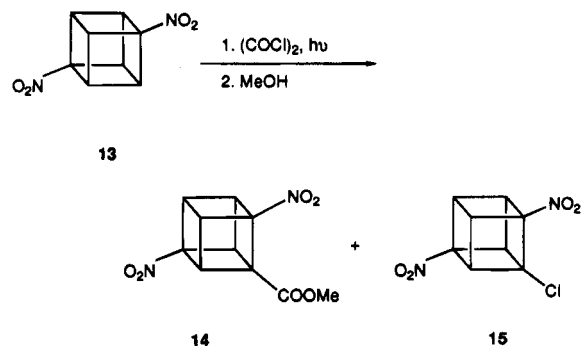
The chlorination might be due to increased concentration of the  $\cdot\text{Cl}$  moiety formed from the cleavage of  $\text{CO}-\text{Cl}$  in oxalyl chloride under the reaction conditions. In free-radical substitution reactions with oxalyl chloride and related derivatives,<sup>13</sup> it is commonly accepted that the overall process is initiated by the dissociation steps outlined in eq 1. Subsequent steps would likely involve abstraction of hydrogen from the substrate molecule by



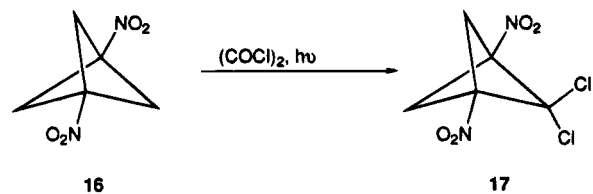
chlorine atom (eq 2) followed by the recombination reaction shown in eq 3. The amounts of chlorinated products increase under Pyrex/sunlamp and reflux conditions. This might be attributed to the predominant carbonyl-chlorine bond cleavage at higher wave lengths (365 nm) and higher temperatures. However, the im-

portance of steric and electronic effects of the polysubstituted cubyl radicals can not be overlooked.

An important application of this methodology is the functionalization of nitrocubanes. Considerable effort in recent years has been directed toward the synthesis of polyfunctionalized nitrocubanes because of their potential use as explosives, propellants, fuels, and binders.<sup>1,14</sup> The use of anionic reactions for the synthesis of substituted nitrocubanes is hampered by the sensitivity of the nitro groups to the reaction conditions. Photochemical reaction of 1,4-dinitrocubane **13** with oxalyl chloride under a sunlamp in Pyrex at room temperature produced, after esterification with methanol, 2-carbomethoxy-1,4-dinitrocubane **14** and 2-chloro-1,4-dinitrocubane **15**, in 48% and 36% yields, respectively.



Increasing the reaction temperature to 60 °C resulted in an increased ratio of chlorinated compound **15** to ester **14**. It is interesting that the photochemical reaction of 1,3-dinitrobicyclo[1.1.1]pentane (**16**) with oxalyl chloride has been reported to give predominantly dichlorinated product **17**.<sup>15</sup>



Significant information was obtained from the X-ray structure determination of tetracarboxymethoxycubane (**8c**),<sup>16</sup> pentacarboxymethoxycubane (**10c**),<sup>16</sup> and 2-carbomethoxy-1,4-dinitrocubane (**14**).<sup>17</sup> Carbon-carbon bond distances between two carbons bearing electron-withdrawing groups are 1.596 Å in **8c**, 1.584 Å in **10c**, and 1.565 Å in **14**. The shortening of the C-C bond bearing adjacent nitro and ester groups in **14** might have some implication for prediction of the densities of polysubstituted cubanes such as octanitrocubane.<sup>14,18</sup>

(14) For the synthesis of 1,3,5,7-tetranitrocubane see: Eaton, P. E.; Xiong, Y.; Gilardi, R. *J. Am. Chem. Soc.* **1993**, *115*, 10195. For the synthesis of 1,4-dinitrocubane see: Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. Eaton, P. E.; Wicks, G. E. *J. Org. Chem.* **1988**, *53*, 5353.

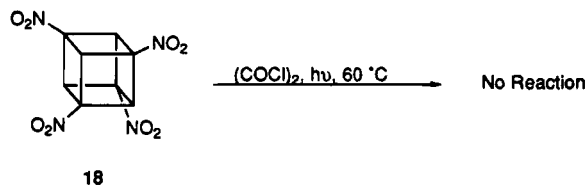
(15) Wiberg, K. B.; Ross, B. S.; Isbel, J. J.; McMurdie, N. *J. Org. Chem.* **1993**, *58*, 1372.

(16) Butcher, R.; Bashir-Hashemi, A.; Gilardi, R. Unpublished results.

(17) Ammon, H. L.; Bashir-Hashemi, A. *Acta. Crystallog.* **1993**, *C49*, 1641.

(13) Kharasch, M. S.; Brown, H. C. *J. Am. Chem. Soc.* **1940**, *62*, 454. Kharasch, M. S.; Brown, H. C. *Ibid.* **1942**, *64*, 329; Freeman, P. K.; Raymond, F. A.; Sutton, J. C.; Kindley, W. R.; *J. Org. Chem.* **1968**, *33*, 1448. Wiberg, K. B.; Williams, V. Z.; *Jr. Ibid.* **1970**, *35*, 369. Applequist, D. E.; Sasaki, T. *Ibid.* **1978**, *43*, 2399.

Attempts at photochemical chlorocarbonylation of 1,3,5,7-tetranitrocubane (**18**) under various reaction conditions failed. The lack of reactivity of tetranitrocubane toward photochemical substitution could be due to a combination of the increased C–H strength relative to cubane and the monosubstituted cubanes (Table 1) and to a high polar effect arising from three nitro groups that surround each C–H position.



In conclusion, a simple and efficient photochemical procedure for the synthesis of polysubstituted cubanes has been developed. This methodology should be applicable to a variety of substituted cage compounds in which functionalization by anionic or cationic reactions is difficult.

### Experimental Section

NMR spectra were recorded on a Bruker or G.E. 300-MHz spectrometer. All chemical shifts are reported in ppm, downfield from internal tetramethylsilane. Mass spectra were measured on a Finnegan OWA 1020B. IR spectra were recorded on a Perkin-Elmer 467 spectrometer. All melting points are uncorrected. Oxalyl chloride (98%) was purchased from Aldrich and used without purification. All cubane derivatives prepared in this article are relatively stable at room temperature. Nevertheless, care should be taken when handling these energetic materials.

**Procedure A.** Cubanecarboxylic acid (**1a**)<sup>2</sup> (1.48 g, 10.0 mmol) and 100 mL of oxalyl chloride were mixed and stirred at room temperature for 30 min. The resulting clear solution was irradiated in a Pyrex flask with a General Electric 275-W sun lamp, held approximately 12 cm from the reaction flask. The reaction temperature was kept between 10 and 20 °C. After 5 h of irradiation, <sup>1</sup>H NMR of the reaction mixture showed the disappearance of the starting material and formation of 1,2-bis(chlorocarbonyl)cubane (**2b**): δ 4.05 (m, 2H); 4.43 (dd, 4H), 1,4-bis(chlorocarbonyl)cubane (**3b**): δ 4.43(s) ppm, and 1,3-bis(chlorocarbonyl)cubane (**4b**): δ 4.82 (m, 2H); 4.45 (m, 2H); 4.15 (m, 2H) ppm, in an approximately 1:1:3 ratio. The irradiation was continued and formation of trisubstituted cubanes **5b**: δ 5.18 (m, 1H), 4.82 (m, 3H), 4.10 (m, 1H), and **7b**: δ 4.86 (m, 2H), 4.50 (t, 2H), 4.43 (m, 1H) ppm, and their transformation to higher substituted cubanes was followed. After 40 h, the very complicated spectrum of the reaction mixture gave rise to the much simpler resonances of 1,3,5,7-tetrakis(chlorocarbonyl)cubane (**6b**): δ 5.20 (s), 1,2,4,7-tetrakis(chlorocarbonyl)cubane (**8b**): δ 4.92 (s), and 1,2,3,7-tetrakis(chlorocarbonyl)cubane (**9b**): δ 5.23 (t, 1H); 4.85 (dd, 2H); 4.63 (t, 1H), in an approximate ratio of 50:15:35. The extension of the reaction time to 70 h only resulted in a 10% decrease of compound **9b** and the appearance of a small peak at 5.21 (s) ppm which is assigned to pentasubstituted cubane **10b**. The excess oxalyl chloride was removed on a rotary evaporator, and the residue was stirred with dry MeOH (50 mL) at room temperature for 3 h. The mixture was concentrated and the oily residue was taken up into EtOAc (30 mL), washed with 5% aqueous Na<sub>2</sub>CO<sub>3</sub> and then brine, and dried (Na<sub>2</sub>SO<sub>4</sub>). After removing the solvent under reduced pressure, the crude product was triturated with ether/hexanes 1:1 and 1,3,5,7-tetracarboxymethoxycubane (**6c**)<sup>14</sup> was isolated as a color-

less solid (1.20 g): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.62 (s, 4H), 3.73 (s, 12H) ppm. The filtrate was concentrated and chromatographed using a Chromatotron (silica gel) and CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1:1 as eluent to give compound **10c** (270 mg, 7%): mp; 114–116 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.64 (s, 3H), 3.73 (s, 9H), 3.71 (s, 3H), 3.69 (s, 3H) ppm; <sup>13</sup>C NMR 168.8, 167.4, 165.2, 61.5, 57.8, 52.3, 52.2, 52.1, 51.7, 49.0 ppm; MS (CI) 395 (M + 1)<sup>+</sup>, 363, 335, 318, 304, 291, 275, 245; IR (KBr) 2960, 1730, 1440, 1310, 1200, 750 cm<sup>-1</sup>. Anal. Calcd for (C<sub>18</sub>H<sub>18</sub>O<sub>10</sub>): C, 54.83; H, 4.60. Found: C, 54.45; H, 4.89.

1,2,4,7-Tetracarboxymethoxycubane (**8c**); (270 mg, 8%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.45 (s, 4H), 3.72 (s, 12H); 1,2,3,7-tetracarboxymethoxycubane (**9c**); (330 mg, 10%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.70 (m, 1H), 4.49 (m, 2H), 4.28 (m, 1H), 3.74 (s, 6H), 3.73 (s, 3H), 3.71 (s, 3H); and 1,3,5,7-tetracarboxymethoxycubane (**6c**): 140 mg (total yield of **6c**, 40%).

Hydrolysis of tetraester **9c** with hot aqueous HCl solution (10%) for 8 h gave 1,2,3,7-cubane tetraacid **9a** in 70% yield: mp 221–223 °C dec; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 4.64 (m, 1H), 4.41 (m, 2H), 4.25 (m, 1H) ppm; IR (KBr) 2500–3500, 1700, 1435, 1310, 1225 cm<sup>-1</sup>.

**Procedure B.** The irradiation of cubanecarboxylic acid (**1a**) (1.48 g, 10.0 mmol) with oxalyl chloride (100 mL) was conducted in a quartz flask with a Rayonet photochemical reactor (1849–2537 Å). The reaction temperature was kept at 35–40 °C. After 8 h of irradiation, <sup>1</sup>H NMR showed the complete conversion of cubanecarboxylic acid (**1a**) to a mixture of 1,3,5,7-, 1,2,4,7-, and 1,2,3,7-tetraacid chlorides **6b**, **8b**, and **9b**, in a ratio of 55:10:35. Compound **6b** can be isolated as a colorless solid in 40–50% yield by triturating the reaction mixture with 10.0 mL of ether. The small resonance at 5.21 ppm for the pentasubstituted isomer **10b** appeared after 18 h of irradiation.

**Irradiation of 1,4-Dicarbomethoxycubane (3c) with Oxalyl Chloride.** A mixture of 1,4-dicarbomethoxycubane (**3c**) (440 mg, 2.0 mmol) in oxalyl chloride (50 mL) was photolyzed in Pyrex under a sunlamp at room temperature. After 16 h, <sup>1</sup>H NMR showed no trace of the remaining starting material. The excess oxalyl chloride was removed on a rotary evaporator and the residue was stirred with dry MeOH (50 mL) at room temperature for 3 h. The mixture was concentrated, and the oily residue was taken up in EtOAc (30 mL), washed with 5% aqueous Na<sub>2</sub>CO<sub>3</sub> then brine, and dried (Na<sub>2</sub>SO<sub>4</sub>). After removing the solvent under reduced pressure, the crude product was triturated with hexanes/ether (5:1) to give 1,2,4-tricarbomethoxycubane (**7c**) (400 mg, 72%): mp 69–72 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.84 (m, 2H), 4.32 (m, 3H), 3.72 (s, 3H), 3.73 (s, 3H), 3.75 (s, 3H) ppm. Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>6</sub>: C, 60.42; H, 5.07. Found: C, 59.88; H, 5.67. In another experiment the reaction time was extended to 72 h. After esterification and the usual workup (vide supra), 1,2,4,7-tetracarboxymethoxycubane (**8c**) was isolated upon triturating with hexanes/ether (3:1) (200 mg, 30%). The filtrate was concentrated and chromatographed using a Chromatotron (silica gel) and CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1:1 as eluent to give an additional 40 mg of **8c** (total yield 36%) and 1,2,3,7-tetracarboxymethoxycubane (**9c**) (300 mg, 45% yield).

**Chlorination of Tetracarboxymethoxycubanes 6c and 8c.** Tetracarboxymethoxycubane **6c** or **8c** (336 mg, 1.0 mmol) in oxalyl chloride (50 mL) was photolyzed in Pyrex under a sunlamp at 60 °C for 48 h. <sup>1</sup>H NMR of the reaction mixture showed no trace of the remaining starting material. The excess oxalyl chloride was removed on a rotary evaporator and the residue was stirred with dry MeOH (50 mL) at room temperature for 3 h. The mixture was concentrated, and the oily residue was taken up in EtOAc (30 mL), washed with 5% aqueous Na<sub>2</sub>CO<sub>3</sub> and then brine, and dried (Na<sub>2</sub>SO<sub>4</sub>). After removing the solvent under reduced pressure, the crude product was chromatographed using silica gel and hexanes/CH<sub>2</sub>Cl<sub>2</sub> (5:1) as eluent to give 3-chloro-1,2,4,7-tetracarboxymethoxycubane (**12c**) (130 mg, 35%): mp 134–135 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.68 (m, 1H), 4.54 (dd, 1H), 4.42 (dd, 1H); 3.80 (s, 6H); 3.78 (s, 6H) ppm. <sup>13</sup>C NMR δ 167.4, 165.4, 68.3, 62.8, 56.0, 53.0, 52.3, 52.2, 48.2, 44.8; IR (KBr) 3000, 1740, 1440, 1200, 800 cm<sup>-1</sup>. Anal. Calcd for (C<sub>16</sub>H<sub>15</sub>ClO<sub>8</sub>): C, 51.83; H, 4.08. Found: C, 51.35; H, 4.60. 2-Chloro-1,3,5,7-tetra-

(18) Bashir-Hashemi, A.; Ammon, H. L.; Choi, C. S. *J. Org. Chem.* **1990**, *55*, 416. For a similar structure see Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232. For a special case see Eaton, P. E.; Pramod, K.; Gilardi, R. *J. Org. Chem.* **1990**, *55*, 5746.

carbomethoxycubane (**11c**) (103 mg, 28%): mp 178–180 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.65 (s, 3H), 3.80 (s, 9H), 3.75 (s, 3H) ppm;  $^{13}\text{C NMR}$   $\delta$  168.6, 166.2, 72.7, 56.8, 52.3, 52.2, 50.9, 49.4 ppm; MSDEP (CI) 390, 388, 364, 355, 354, 334. GC Mass spectra of the reaction mixture shows a small amount of dichloro-tetracarbomethoxycubane.

**Irradiation of 1,4-Dinitrocubane (13).** A mixture of 1,4-dinitrocubane (**13**)<sup>14</sup> (388 mg, 2.0 mmol) in oxalyl chloride (50 mL) was photolyzed in Pyrex under a sunlamp for 18 h at room temperature. Oxalyl chloride was removed on a rotary evaporator and the solid residue was partitioned between EtOAc (40 mL) and NaOH solution (5%, 30 mL). After stirring for 3 h, the organic phase was separated, washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was chromatographed on silica gel using hexanes/ $\text{CH}_2\text{Cl}_2$  (1:1) to give 2-chloro-1,4-dinitrocubane (**15**) (164 mg, 36%): mp 145–147 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.84 (m, 2H); 4.71 (m, 3H); IR (KBr) 1530, 1360, 1200, 800  $\text{cm}^{-1}$ . Anal. Calcd for ( $\text{C}_8\text{H}_5\text{ClN}_2\text{O}_4$ ) C, 42.03; H, 2.20. Found: C, 41.78; H, 2.31.

The alkaline layer was acidified with HCl (10%), and organic materials were extracted with EtOAc (2  $\times$  30 mL). The organic phase was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated by rotary evaporator to give 230 mg of a crude product which was triturated with hexanes/acetone 10:1 (5.0 mL) to give 2-carboxy-1,4-dinitrocubane (**14a**) mp 187–189

°C dec;  $^1\text{H NMR}$  (acetone- $d_6$ )  $\delta$  4.96 (m, 2H); 4.74 (m, 3H) ppm;  $^{13}\text{C NMR}$   $\delta$  206.8, 86.2, 84.1, 77.5, 51.8, 50.2, 48.0.

2-Carboxy-1,4-dinitrocubane (**14a**) (100 mg, 0.4 mmol) was stirred with MeOH (20 mL) and  $\text{CH}_3\text{SO}_3\text{H}$  (4 drops) at reflux overnight. The reaction mixture was concentrated and then dissolved in EtOAc (20 mL). The solution was washed with aqueous  $\text{Na}_2\text{CO}_3$  (5%) and then brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was triturated with ether/hexanes (1:1) to give 2-carbomethoxy-1,4-dinitrocubane (**14c**): mp 165–167 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  4.92 (m, 2H); 4.62 (m, 3H), 3.80 (s, 3H). Anal. Calcd for ( $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_6$ ) C, 47.63; H, 3.20. Found: C, 47.47; H, 3.53.

In another experiment, the irradiation was conducted at 60 °C for 18 h in Pyrex under sunlamp and after the usual workup, the yield of 2-chloro-1,4-dinitrocubane (**15**) was increased to 42%. The isolated yield of 2-carbomethoxy-1,4-dinitrocubane (**14c**) was only 10%. Mass spectra of the reaction mixture showed a substantial amount of dichloro isomers are formed.

**Acknowledgment.** Support provided by ARDEC to GEO-CENTERS, INC. and by the Office of Naval Research to the Univ. of Maryland is gratefully appreciated.

JO941498O