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CRYSTAL AND MOLECULAR STRUCTURES OF DIMESITYLKETENE AND BIS(3,5-DIBROMO-2,4,6-TRIMETHYLPHENYL)KETENE. INTRINSIC TORSIONAL ANGLES AND BUTTRESSING EFFECTS IN 1,1-DIMESITYLVINYL PROPELLERS

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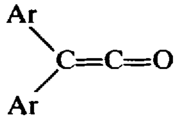
ABSTRACT

The crystal and molecular structures of dimesitylketene (**1**) and bis(3,5-dibromo-2,4,6-trimethylphenyl)ketene (**2**), the first free ketenes to be studied by X-ray diffraction, have been determined. The molecules of **1** and **2** have crystallographic C_1 and C_2 symmetry, respectively, and exist in a propeller conformation. Molecular mechanics calculations of **1** and **2** using a modification of Allinger's new allene parameters reproduce satisfactorily the structural parameters of the ketenes. The torsional angles of the aryl rings in **1** and **2** are similar (*ca.* 50°) and are regarded as 'intrinsic' values for a 1,1-dimesitylvinyl propeller. From the similarity in aryl torsional angles in **1** and **2** it is concluded that the buttressing effects in **2** (if any) are not markedly manifested in the structural parameters of **2**.

INTRODUCTION

Conspicuously missing within the host of organic functional groups structurally characterized in the solid state is the ketene functionality.[1] This is hardly surprising since the parent compound and its alkyl derivatives exist as liquids at room temperature, and some ketenes are extremely reactive and prone to dimerization.[2] Consequently, most of the structural data on ketenes available to date relies on spectroscopic (microwave, infrared and Raman) data. In contrast with their 'simple' counterparts, some ketenes substituted by bulky aryl groups (such as dimesitylketene (**1**)[3] which is an important intermediate in the synthesis of crowded β,β-dimesityl substituted stable simple enols)[4] have sufficient kinetic stability to allow their routine handling and purification, and are crystalline solids at room temperature.



1 Ar = 2,4,6-$Me_3C_6H_2$

2 Ar = 3,5-Br_2-2,4,6-Me_3C_6

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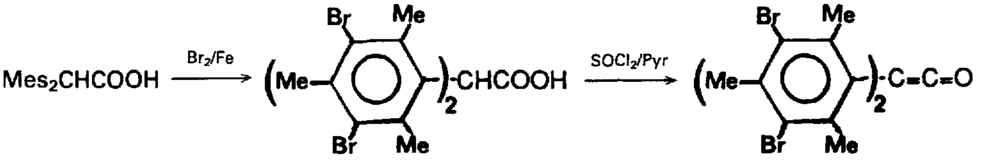
In the present work we describe the crystal and molecular structure of the known dimesitylketene **1** and the new bis(3,5-dibromo-2,4,6-trimethylphenyl)ketene (**2**). Our interest in the structures of these compounds was threefold: (a) to obtain accurate structural data on the relatively unknown ketene functionality (b) to find out whether the diarylvinyl moiety exist in a propeller conformation[5] where the two rings are twisted in the same sense (c) to assess whether the buttressing effect of the bromine atoms on the methyl groups of **2** is manifested in the geometry and conformation of **2**. The third topic is of particular interest in light of the recent claim that the buttressing effects make the pentamethylphenyl group effectively bulkier than a mesityl ring which enables the kinetic stabilization of acid enols.[6]

RESULTS AND DISCUSSION

Ketene **1** was prepared according to a modification[5a] to Fuson's method.[3] Ketene **2** was synthesized in two steps from the known dimesitylacetic acid via electrophilic bromination and treatment of the resulting tetrabromo acid with $SOCl_2$ and pyridine, equation (1). Ketene **2** was characterized by a ν_{max}(nujol) at 2100 cm^{-1} in the IR spectrum and by its analysis, spectra and MS fragmentation pattern (see experimental section).



(1)

Mes = 2,4,6-$Me_3C_6H_2$

X-ray data for crystals of **1** and **2** grown from petroleum ether at 278 K were collected at room temperature. Crystals of **1** are monoclinic, space group $P2_1/c$ with four molecules per unit cell located in general positions, whereas crystals of **2** are orthorhombic, space group *Pccn* with four molecules per unit cell located along the crystallographic C_2 axes. Final atomic parameters are listed in Table 1 and 2 and selected structural parameters are collected in Table

Table 1. Positional parameters and estimated standard deviations for 1

Atom	X	Y	Z	Atom	X	Y	Z
O	0·6926(9)	−0·180(1)	0·3744(3)	C(11)	0·4067(9)	0·229(1)	0·4746(4)
C(1)	0·653(1)	−0·043(1)	0·3801(4)	C(12)	0·5061(9)	0·192(1)	0·3475(3)
C(2)	0·6184(9)	0·107(1)	0·3887(3)	C(13)	0·361(1)	0·120(1)	0·3273(4)
C(3)	0·6881(9)	0·178(1)	0·4424(3)	C(14)	0·254(1)	0·217(1)	0·2946(4)
C(4)	0·857(1)	0·184(1)	0·4530(3)	C(15)	0·287(1)	0·371(1)	0·2809(4)
C(5)	0·918(1)	0·259(1)	0·5014(4)	C(16)	0·433(1)	0·437(1)	0·2970(3)
C(6)	0·818(1)	0·330(1)	0·5397(4)	C(17)	0·545(1)	0·350(1)	0·3301(3)
C(7)	0·654(1)	0·321(1)	0·5298(4)	C(18)	0·318(1)	−0·049(1)	0·3415(4)
C(8)	0·588(1)	0·245(1)	0·4818(4)	C(19)	0·160(1)	0·477(1)	0·2490(5)
C(9)	0·972(1)	0·114(1)	0·4121(4)	C(20)	0·707(1)	0·425(1)	0·3439(4)
C(10)	0·885(1)	0·410(1)	0·5938(4)				

Estimated standard deviations in the least significant digits are shown in parentheses.

Table 2. Positional parameters and estimated standard deviations for **2**

Atom	X	Y	Z	Atom	X	Y	Z
Br(1)	0·2701(2)	1·1272(1)	0·5345(1)	C(5)	0·330(1)	1·000(1)	0·560(1)
Br(2)	0·5851(2)	0·8672(1)	0·7421(1)	C(6)	0·418(1)	0·985(1)	0·6308(9)
O	0·250	0·750	0·306(1)	C(7)	0·456(1)	0·8915(9)	0·6470(9)
C(1)	0·250	0·750	0·387(1)	C(8)	0·409(1)	0·8152(9)	0·5952(8)
C(2)	0·250	0·750	0·473(1)	C(9)	0·170(1)	0·947(1)	0·431(1)
C(3)	0·312(1)	0·8322(8)	0·5259(9)	C(10)	0·466(2)	1·069(1)	0·688(1)
C(4)	0·271(1)	0·9268(9)	0·5062(8)	C(11)	0·467(1)	0·7163(9)	0·608(1)

Estimated standard deviations in the least significant digits are shown in parentheses.

3. Stereoviews of the crystal structures of **1** and **2** and the numbering schemes are shown in Figures 1 and 2, respectively.

A search in the Cambridge Structural Database revealed that all the 34 ketenic structures reported up to June 1986 correspond to organometallic derivatives in which the ketene moiety is ligated to a metal. Structures **1** and **2** therefore represent the first structures of uncoordinated ketenes determined by X-ray crystallography.[7]

As the Figures show, ketenes **1** and **2** exist in a chiral propeller conformation in which both rings are twisted in the same sense. In both cases the torsional angles of the rings are appreciable (48·8° and 56·8° for **1**, 51·8° for both rings of **2**). Of special interest in **1** and **2** are the ketenic C=O and C=C bond lengths. As Table 3 shows, the C=O bond lengths are

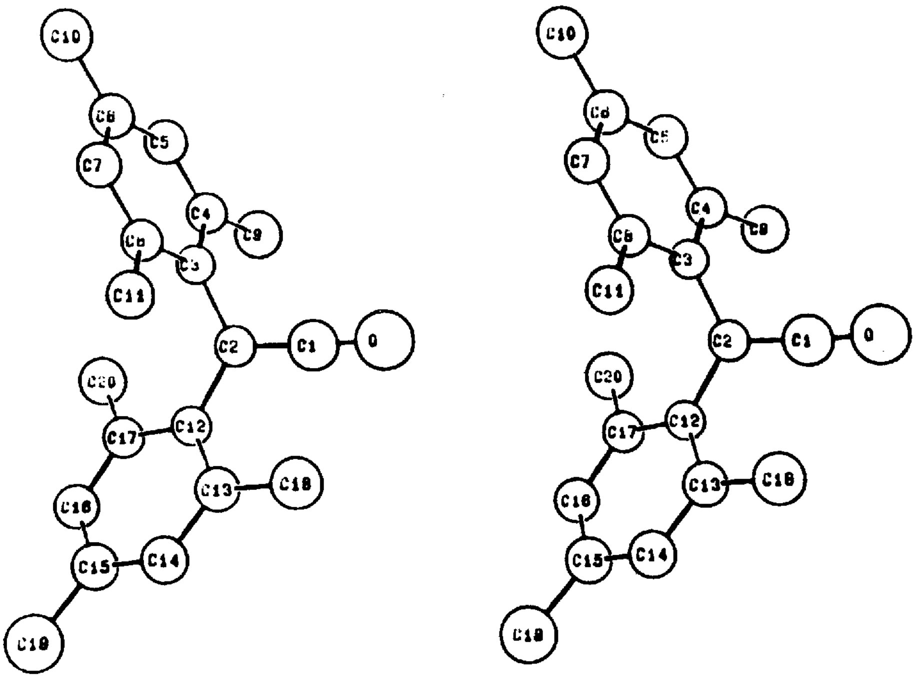


Figure 1. Stereoview and numbering scheme of the X-ray structure of dimesitylketene (**1**)

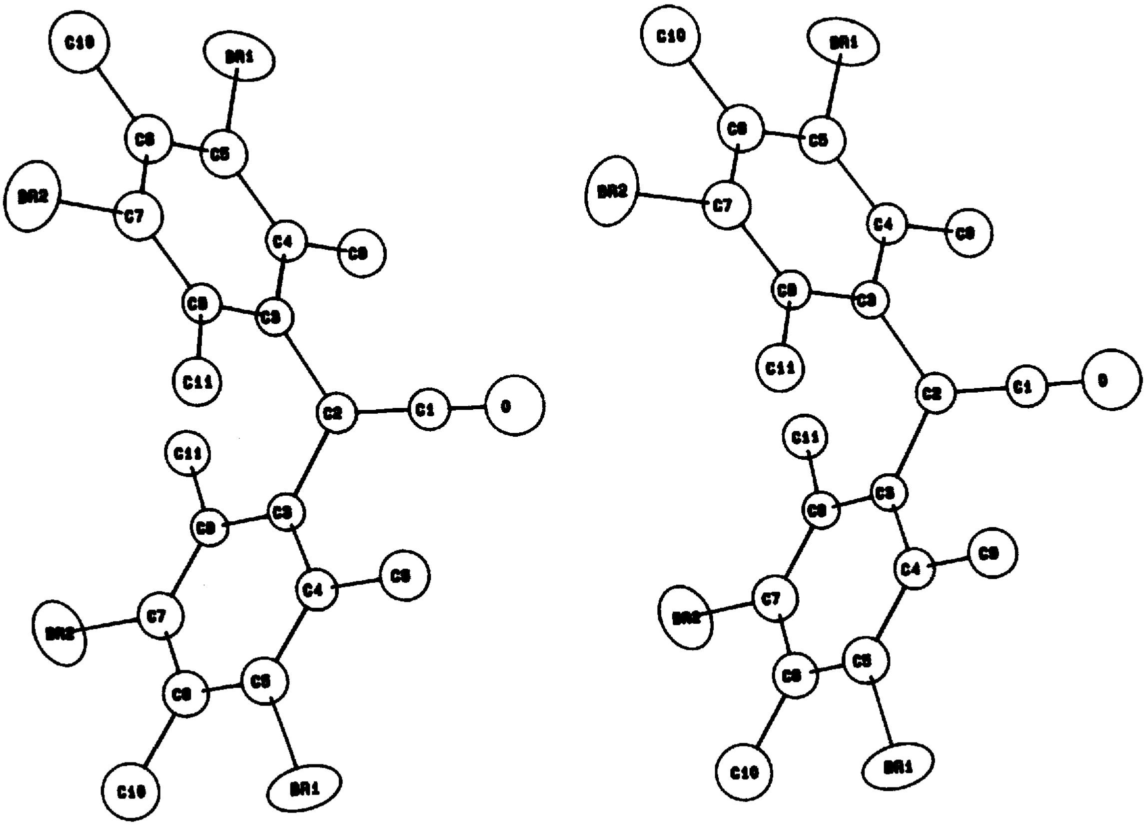


Figure 2. Stereoview and numbering scheme of the X-ray structure of bis(3,5-dibromo-2,4,6-trimethylphenyl)ketene (2)

1·18(1) Å and 1·17(3) Å and the C═C bond lengths are 1·29(1) and 1·25(3) Å, respectively, and therefore they are pairwise identical within experimental error. These C═C bond lengths are somewhat shorter than the values found by microwave spectroscopy for the parent ketene,[8] and for methylketene[9] and dimethylketene[10] (1·314, 1·306 and 1·314 Å respectively) whereas the C═O bond lengths for all the aforementioned ketenes are similar. The C═C═O angle is 176° and 180·0° for **1** and **2**, respectively. The small deviation from linearity in the case of **1** is the result of the local C_1 symmetry of the C═C═O moiety: this unit will be linear only if it lies on a C_2 axis of symmetry. The linearity (or near linearity) of the CCO atoms is in contrast with the usually observed nonlinear arrangements in organometallic derivatives of diphenylketene: for example in bis(η-5-cyclopentadienyl)-(diphenylketene-C,O)-vanadium the CCO angle is 135·9(5)°.[7c]

Molecular mechanics calculations

In order to find out whether the aryl torsional angles experimentally found for **1** and the different symmetries found in the crystal for **1** and **2** represent the minimum energy

Table 3. Selected experimental and calculated structural parameters for **1** and **2**[a]

Atoms	**1** exp	**1** calcd	**2** exp	**2** calcd
O—C(1)	1·18(1)	1·17	1·17(3)	1·17
C(1)—C(2)	1·29(1)	1·29	1·25(3)	1·29
C(2)—C(3)	1·49(1)	1·48	1·51(1)	1·48
C(2)—C(12)	1·50(1)	1·48	1·51(1)	1·48
C(3)—C(4)	1·42(1)	1·41	1·42(2)	1·41
C(12)—C(13)	1·42(1)	1·41	1·42(2)	1·41
C(3)—C(8)	1·40(1)	1·41	1·40(2)	1·41
C(12)—C(17)	1·40(1)	1·41	1·40(2)	1·41
C(4)—C(9)	1·51(1)	1·51	1·51(2)	1·52
C(13)—C(18)	1·48(1)	1·51	1·51(2)	1·52
C(8)—C(11)	1·52(1)	1·51	1·51(2)	1·52
C(17)—C(20)	1·51(1)	1·51	1·51(2)	1·52
O—C(1)—C(2)	176 (1)	179·9	180·0	179·9
C(1)—C(2)—C(3)	115·5(8)	119·3	120·2(8)	119·1
C(1)—C(2)—C(12)	119·3(8)	118·8	120·2(8)	118·9
C(2)—C(3)—C(4)	120·5(7)	120·1	120(1)	120·4
C(2)—C(12)—C(13)	121·4(8)	120·2	120(1)	119·8
C(2)—C(3)—C(8)	120·0(7)	120·9	120(1)	120·1
C(2)—C(12)—C(17)	118·7(7)	120·6	120(1)	120·6
C(3)—C(4)—C(9)	122·3(8)	122·6	121(1)	121·2
C(12)—C(13)—C(18)	122·3(8)	122·1	121(1)	120·0
C(3)—C(8)—C(11)	121·2(8)	122·4	120(1)	120·7
C(12)—C(17)—C(20)	122·3(8)	122·6	120(1)	121·2
$\mathrm{Ar_1}$—C═C[b]	48·8	50·0	51·8	51·1
$\mathrm{Ar_2}$—C═C[b]	56·8	51·4	51·8	52·1

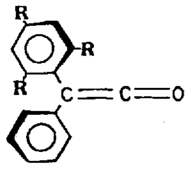
[a] Bond lengths in angstroms, angles in degrees.
[b] Dihedral angle.

conformation of the molecules or they are due to packing forces in the crystal, we resorted to molecular mechanics calculations. Allinger's latest force field program (MM2(85)[11]) does not implement ketene parameters, and therefore we modified the recently published allene parameters.[12] Two different conformations were used as input geometries: one having identical torsional angles for the aryl rings (60°, C_2 symmetry) and the other having 0° and 90° torsional angles (C_s symmetry). In both cases the input structures relaxed into a propeller conformation having approximately C_2 symmetry. The calculated structural parameters for **1** and **2** are collected in Table 3. In general there is satisfactory agreement between the calculations and the X-ray structures. Most of the bond lengths are correctly reproduced although the aryl—C═C bonds are somewhat underestimated (calculated: 1·48 Å, experimental: 1·49–1·51 Å). The calculated average torsional angles for the aryl rings in **1** and **2** are similar: 50·7° for **1** and 51·6° for **2**. It can be concluded from the calculations that for **1** and **2** the minimum energy conformation corresponds to a propeller conformation of C_2 symmetry.

Intrinsic torsional angles in dimesitylvinyl propellers

We have shown recently that 1-alkyl-2,2-dimesitylethenols **3** exist in a propeller conformation in which the torsional angles of the mesityl rings increase with the increased bulk of R. A linear correlation was found between the torsional angles of the ring *cis* to R in **3** and Taft's steric parameters E_s of R.[13] Since both torsional angles in the dimesitylvinyl moiety are strongly influenced by the double bond substituent it was of interest to find out what the angles are when the size of the substituent is reduced. With this purpose in mind, we recently determined the X-ray structure of 1,1-dimesitylethylene (**4**)[14] in which the two double bond substituents are hydrogens, the smallest possible substituents. Since the molecule is located in the crystal on a site of local C_1 symmetry compound **4** exists in the solid state in a propeller conformation with different aryl torsional angles of 50° and 58°. A further step in that direction is ketene **1**, where the *sp* hybridization of the central carbon puts the double bond substituent (the ketene oxygen) in a linear or a nearly linear arrangement with the vinylic carbons. The substituent-aryl rings interactions (if any) in this case are substantially reduced. Hence, the mesityl torsional angles of **1** can be considered as the 'intrinsic' torsional angles of a dimesitylvinyl moiety (i.e. the angles for an isolated dimesitylvinyl moiety without any double bond substituent). The X-ray structure and the calculations of **1** indicate that even when the double bond substituents *cis* to the mesityl rings are absent, these angles are appreciable (*ca.* 50°). Moreover, the propeller conformation of the rings found for **1** (and **2**) suggest that a propeller arrangement is the preferred conformation for an isolated dimesitylvinyl moiety. Finally, we would like to point out that from the geometrical point of view stable diarylketenes (e.g. **5**) can in principle serve as models for the aryl torsional angles of the short-lived vinyl cations (such as **6**)[15] and help predict the stereochemistry of its capture by nucleophiles when the two rings are differently substituted as in **5** and **6**. (Work is in progress to test this idea.)

$$\begin{array}{lll} \mathrm{Mes_2C{=}C(X)R} & \mathbf{3}\ \ X = OH & R = \mathrm{Me,Et,i\text{-}Pr,}t\text{-}\mathrm{Bu} \\ & \mathbf{4}\ \ X = R = H & \end{array}$$



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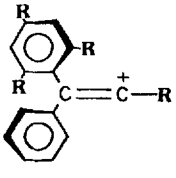

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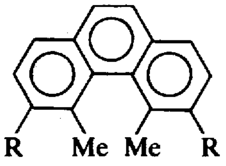
Buttressing effects in mesityl rings

Buttressing interactions are normally invoked whenever the formal introduction of a bulky substituent (e.g. a methyl group) on a position *not* directly involved in steric interaction results in a substantial increase of the internal strain in the ground state and/or in the transition state of a dynamic process or reaction.[16] These effects were first observed by Chien and Adams[17] who reported that 3′-substituted 2-nitro-6-carboxy-2′-methoxybiphenyls (3′-substituent = OMe, Me, Cl, Br, NO_2) are more stable to racemization than the unsubstituted compounds or the corresponding 5′-substituted derivatives. The name 'buttressing effect' for this phenomenom was coined by Rieger and Westheimer[18] who calculated and experimentally determined the buttressing effects in the racemization of 2,2′,3,3′-tetraiodo-5,5′-dicarboxybiphenyl. The activation energy for racemization of the tetraiodo compound was 6·4 kcal mol^{-1} higher than that for 2,2′-diiodo-5,5′-dicarboxybiphenyl. Buttressing effects need not always result in an increased barrier, 'reverse buttressing effects' are known in which the formal introduction of a buttressing group leads to a drop of a rotational barrier.[19] In a recent detailed analysis of buttressing effects in phenanthrenes **7** and **8** it was shown that the replacement of the 3,6 hydrogens of **7** by methyl groups results in dynamic and structural buttressing effects. The enantiomerization barrier of 16·1 kcal mol^{-1} for **7** is raised to 23·1 kcal mol^{-1} for **8**,[20] and the torsional angle defined by the internal methyl groups and the carbons attached to them was increased from 67·4° in **7** to 73·3° in **8**. Phenanthrene **8** therefore represents a system in which the buttressing effects are clearly manifested both in the ground state and in the transition state.



7 R = H
8 R = Me

Recently, O'Neill and Hegarty reported that the use of the pentamethylphenyl group 'whose effective size is increased by the buttressing effect of the *m*-Me groups'[6] provided sufficient steric hindrance to render the acid enol **9** kinetically stable. Since the relative stability of **9** *per se* is not evidence for the operation of buttressing effects without comparison with the relative stability of the dimesityl analogue **10** the structural parameters (cf. **7** and **8** above) are of interest.

$Ar_2C{=}C(OH)_2$ **9** Ar = 2,3,4,5,6-Me_5C_6
10 Ar = Mes

Our X-ray results and calculations on **1** and **2** suggest that buttressing effects (if present) are not markedly manifested in the ground state of **2**. This result suggests that the buttressing effect on bis(pentamethylphenyl)ketene should also be minor, since Br and Me are of similar steric requirement (in fact bromine is considered larger than methyl by most radii scales).[21] From the lack of marked manifestations of buttressing effects in the structure of **2** we have to conclude that, at present, more evidence is needed to support the suggestion that buttressing effects play any part in the kinetic stability of **9**.

Conclusions

X-ray diffraction and molecular mechanics calculations of **1** and **2** indicate that these compounds exist in a propeller conformation, in which both rings are twisted in the same sense. The torsional angles of the aryl rings in **1** and **2** are similar (*ca.* 50°) and are regarded as 'intrinsic' values for a 1,1-dimesitylvinyl propeller. From the similarity in aryl torsional angles in **1** and **2** it is concluded that the buttressing effects (if any) are not markedly manifested in the structural parameters of **2**.

EXPERIMENTAL SECTION

Melting points are uncorrected. UV spectra were measured with a Kontron Uvikon 860 spectrometer, and infrared spectra were taken with a Perkin-Elmer 457 G spectrometer. The X-ray diffraction of single crystals of **1** and **2** were measured on a PW 1100 Philips four-circle computer-controlled diffractometer equipped with a fine-focus Mo X-ray tube and a graphite crystal monochromator in the incident beam. Crystallographic data for **1** and **2** are collected in Table 4. ^{1}H spectra were recorded on a Bruker WH-300 pulsed FT spectrometer. In the molecular mechanics calculations the following parameters were used ((44) represents the ketenic C═O carbon): Stretching: 2–44 k_s = 10·50 l_o = 1·28; 6–44: k_s = 10·80 l_o = 1·17; Bending: 2–44–6 k_s = 0·40 180° (identical to C_{sp^3}–C_{allene}–C_{sp^2}) 2–2–44 k_s = 0·47 122·0° (identical to C_{sp^3}–C_{sp^2}–C_{allene}). Torsional 2–2–2–44 $V_1 = -0{\cdot}44$ $V_2 = 0{\cdot}24$ $V_3 = 0{\cdot}06$ (identical to C_{sp^3}–C_{sp^3}–C_{sp^2}–C_{allene}).

Table 4. Crystalographic data for **1** and **2**

	1	**2**
space group	$P2_1/c$	Pccn
a, Å	8·350(3)	9·845(2)
b, Å	8·245(3)	14·063(3)
c, Å	23·617(6)	14·440(3)
β, deg	92·71(5)	90·0
V, Å^3	1624·1(8)	1999·2(7)
z	4	4
ρ calcd, g cm^{-3}	1·14	1·97
μ (Mo Kα), cm^{-1}	0·31	78·86
no. of unique reflections	2061	1269
no. of reflections with $I \geq 3\sigma(I)$	996	698
R	0·093	0·053
R_w	0·108	0·061

Bis(3,5-dibromo-2,4,6-trimethylphenyl)acetic acid

To a stirred mixture of dimesitylacetic acid[22] (4·15 g, 14 mmol) and granular (mesh 60) iron (0·16 g, 2·9 mmol) in CCl_4 (40 ml), was added bromine (3 ml, 58·5 mmol) dropwise in the dark. The mixture was stirred for 24 h at room temperature. To the dark red solution a dilute aqueous sodium thiosulfate solution was added until the disappearance of the color of bromine. Water (200 ml) and CCl_4 (100 ml) were added and after filtration, the organic phase was separated. On evaporation of the solvent, the crude solid acid (7·7 g, 90%) mp 201–202 °C was obtained. Crystallization from methanol gave white needles of bis(3,5-dibromo-2,4,6-trimethylphenyl)acetic acid, mp 218–219 °C.

UV, λ_{max} (hexane): 232 nm (ε = 1060), 277 (930); IR, ν_{max} (nujol) 2900–2600 (w), 1705 (vs,COOH) cm^{-1}; NMR δ ($CDCl_3$) 2·29 (12H, s, *o*-Me), 2·71 (6H, s, *p*-Me), 5·65 (1H, s, CH); MS (165 °C, 70 eV) *m/z* (relative abundance, assignment) 616, 614, 612, 610, 608 (6: 21: 31: 22: 5·6, M); 572, 570, 568, 566, 564 (13: 42: 60: 40: 10, M − CO_2); 534, 532, 530, 528 (20: 54: 55: 18, M − HBr); 475, 473, 471, 469 (12: 32: 32: 13, M − HBr − Me − CO_2), 394, 392, 390 (37: 65: 33, M − HBr − Br − Me − CO_2); 336, 334, 332 (25: 49: 24, M − Br_2Mes − H); 328, 326 (51: 47, M − HBr − 2Br − CO_2); 292, 290, 288 (51, B, 50, Br_2MesCH); 279, 277, 275 (15: 28: 17, Br_2Mes). No signals were detected corresponding to M − 2Br or M − 3Br. Anal. calcd for $C_{20}H_{20}Br_4O_2$: C, 39·25; H, 3·29; Br 52·53. Found: C, 38·93; H, 3·27; Br, 52·09%.

Bis(3,5-dibromo-2,4,6-trimethylphenyl)ketene (2)

To a moisture protected flask containing bis(3,5-dibromo-2,4,6-trimethylphenyl)acetic acid (0·94 g, 1·54 mmol) in dry toluene (7 ml), thionyl chloride (0·4 ml, 5·35 mmol) and dry pyridine (0·1 ml) were added. After 3 h reflux the reaction mixture was cooled to room temperature, dry ether (15 ml) was added and the white precipitate of pyridinium hydrochloride was filtered. After standing for two days under a dry atmosphere yellow crystals of **2** formed (317 mg, 35%), mp 199 °C.

UV, λ_{max} (hexane): 232 nm ($\varepsilon = 2650$), 280 (4300), 370 br (430); IR, ν_{max} (nujol) 2100 cm^{-1} (C=C=O); NMR δ ($CDCl_3$) 2·31 (12H, s, *o*-Me), 2·69 (6H, s, *p*-Me); MS (170 °C, 70 eV) *m/z* 598, 596, 594, 592, 590 (12: 48: 71: 49: 13, M); 474, 472, 470, 468 (33: 98, B, 35, M − Br − CH_2CO). Anal. calcd. for $C_{20}H_{18}Br_4O$: C, 40·40; H 3·03; Found: C, 41·00; H, 2·96%.

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