3314 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *56*, *3314—3318 (1983)* [Vol. 56, No. 11

A Rubrene Problem. Reaction of 3,3,4,4-Tetrabromo-1,2-bis(diphenylmethylene)cyclobutane and Dichloroacetic Acid

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(Received March 10, 1983)

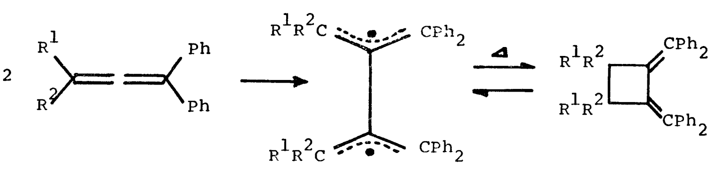
Heating of 3,3,4,4-tetrabromo-1,2-bis(diphenylmethylene)cyclobutane in dichloroacetic acid afforded bridgehead olefin, 7-bromo-1,4,8-triphenyl-2,3-benzobicyclo[3.3.0]octa-2,4,7-trien-6-one, and spiroketone, 2-bromo-2′,3-diphenylspiro[1*H*-indene-1,1′(4′*H*)-naphthalen]-4′-one (**13**). Mechanism of the reaction was discussed. X-Ray structural study of the spiroketone **13** was also reported.

Formation of the bisallyl diradical intermediate (**2a**) in dimerization of chlorotriphenylallene (**1a**) or in thermal ring-cleavage of 3,4-dichloro-3,4-diphenyl-1,2-bis(diphenylmethylene)cyclobutane (**3a**) is the key-step of the *rubrene reaction* which finally gives so-called *rubrene*, 5,6,11,12-tetraphenylnaphthacene (**4a**).[1)] We studied thermal reaction of 3,3,4,4-tetrabromo-1,2-bis(diphenylmethylene)cyclobutane (**3b**)[2)] in expectation of the formation of 5,11-dibromo-6,12-diphenylnaphthacene (**4b**) via the bisallyl diradical intermediate (**2b**), and we found that **3b** is thermally stable but heating of **3b** in dichloroacetic acid affords bridgehead olefin, 7-bromo-1,4,8-triphenyl-2,3-benzobicyclo[3.3.0]octa-2,4,7-trien-6-one (**8a**) and spiroketone, 2-bromo-2′,3-diphenylspiro[1*H*-indene-1,1′(4′*H*)-naphthalen]-4′-one (**13**).

Heating of **3b** in dichloroacetic acid at 120 °C for 1 h gave **8a** and **13** in 30 and 36% yields, respectively. Plausible reaction pathways are shown in Scheme 1. Intermediacy of **5** and **6** was proven by preparing these by separate method. Heating of **3b** in benzene containing a small amount of conc H_2SO_4 under reflux for 7 h gave 7,8,8-tribromo-2,5,5-triphenyl-3,4-benzobicyclo[4.2.0]octa-1,3,6-triene (**5**) in 44% yield. Treatment of **5** with $AgClO_4$ in THF–MeOH gave 7,8-dibromo-5-methoxy-2,5,6-triphenyl-3,4-benzobicyclo[4.2.0]octa-1,3,7-triene (**6b**) in 81% yield. Heating of **5** in dichloroacetic acid for 30 min at 120 °C gave **8a** and **13** in 32 and 35% yields, respectively. Similar heating of **6b** gave **8a** in 88% yield. In the reaction of **5**, rearrangement of phenyl group which leads to **6** is probably competing with that of bromine atom which does to **9**. This was clarified by the reaction of the chloro-analog of **3a** (**3c**) in dichloroacetic acid which gives only the chloro-analog of **8a** (**8b**) in 90% yield. Much easier rearrangement of Br than Cl on four-membered ring has been reported.[3)] Formation of cyclopropenyl-substituted indene intermediate such as **11** seems to be necessary for the conversion of **3** into **13**.

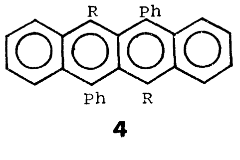
Due to distorted bridge-head olefinic linkage, **8** is reactive and shows interesting reactions. $KMnO_4$ oxidation of **8a** occurred vigorously at room temperature and 2-bromo-1,3,4-triphenylnaphthalene (**17**)[4)] was obtained in 60% yield. A plausible reaction pathway is shown in Scheme 2. Ring-reconstruction of the carbonium ion intermediate (**14**) which was initially formed by an attack of hydroxyl cation on the distorted double bond of **8a** gives cyclic diketone (**16**) *via* **15**, which on decarbonylation finally affords **17**. Michael-type additions of MeOH by a base-catalyzed reaction and of benzene by an $AlCl_3$-catalyzed one to **8a** easily gave 7-bromo-4-methoxy-1,4,8-triphenyl-2,3-benzobicyclo[3.3.0]octa-2,7-dien-6-one (**18a**) and 7-bromo-1,4,4,8-tetraphenyl-2,3-benzobicyclo[3.3.0]octa-2,7-dien-6-one (**18b**), respectively.

From the viewpoint of structural resemblance of **13** to one bioactive component of *Cannabis sativa L*, cannabispirenone-B (**19**),[5)] studies of crystal structure of **13** are interesting subjects. X-Ray crystallographic



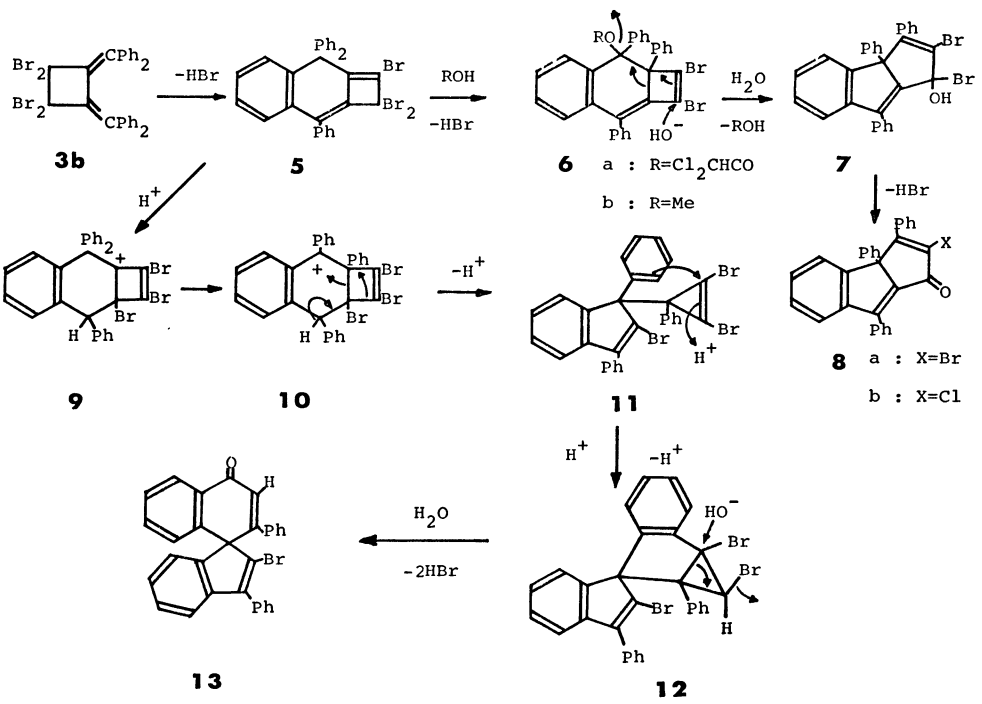
1 **2** **3**

a : R^1=Ph, R^2=Cl
b : R^1=R^2=Br
c : R^1=R^2=Cl

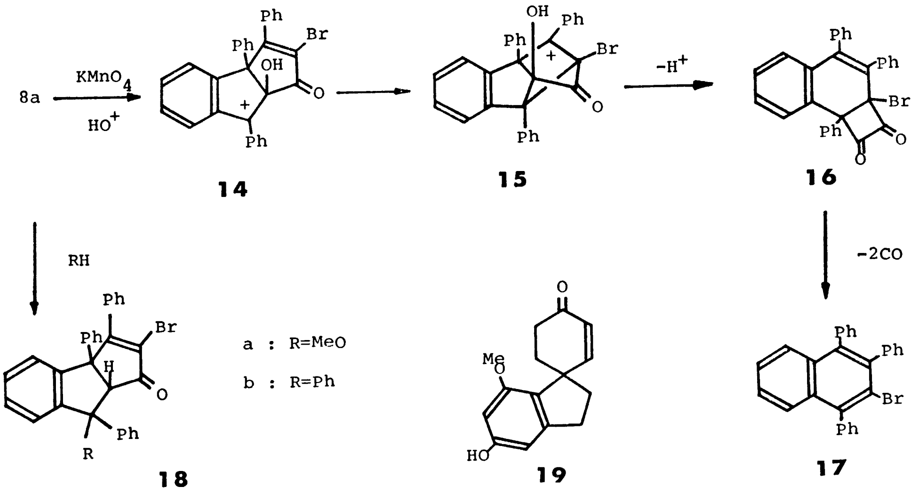


4

a : R=Ph
b : R=Br



Scheme 1.



Scheme 2.

data are shown in Tables 1—5, and perspective view of **13** is shown in Fig. 1. Angles between the following two ring planes are shown in parentheses, A-C (55.3), B-C (3.6), C-E (89.6), D-F (50.4), and E-F (6.0°). These data show that two spiro rings are almost perpendicular each other. Distances between Br and the following atoms are shown in parentheses, C6 (3.42), C10 (3.37), C15 (3.79), and C25 (3.62 Å). However, absolute configuration of **13** was not determined.

Experimental

All the melting points are uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$, respectively. The mass spectra were obtained with an ionization energy of 75 eV.

*Thermal Reaction of 3,3,4,4-Tetrabromo- (**3b**) and 3,3,4,4-Tetrachloro-1,2-bis(diphenylmethylene)cyclobutane (**3c**) in Dichloroacetic Acid.* A solution of **3b** (5.6 g) in dichloroacetic acid (100 ml) was heated at 120 °C for 1 h. The crude solid obtained by addition of water to the reaction mixture was filtered and dried. Recrystallization of the solid from ethyl acetate gave yellow and colorless crystals, which were separated mechanically. Recrystallization of the former from ethyl acetate gave **8a** (1.14 g, 30%) as yellow prisms, mp 185—186 °C; IR 1690 cm^{-1} (C=O); UV 244 (23,400), 289 (14,100), and 364 nm (ε, 8900); ^{13}C NMR δ 70.5 (CPh); MS (m/e) 476 and 474 (M$^+$). Found: C, 75.73; H, 3.85%. Calcd for $C_{30}H_{19}OBr$: C, 75.80; H, 4.03%. Recrystallization of the latter from ethyl acetate gave **13** (1.37 g, 36%) as colorless needles, mp 197—198 °C; IR 1645 cm^{-1} (C=O); UV 243 (23,400), 270sh (15,600), and 283 nm (ε, 16,200); ^{13}C NMR δ 65.0 (spiro C); S (m/e) 476 and 474 (M$^+$). Found: C, 75.59; H, 4.11%. Calcd for $C_{30}H_{19}OBr$: C,

Table 1. Atomic coordinates and e.s.d.'s ($\times 10^4$) of non hydrogen atoms

Atom	x	y	z
Br	5646(1)	2502(1)	338(1)
O	7797(5)	449(3)	6571(7)
C(1)	4092(5)	2378(4)	1447(6)
C(2)	2729(5)	2744(3)	987(6)
C(3)	1880(5)	2439(5)	2208(6)
C(4)	2795(5)	1884(3)	3431(7)
C(5)	4360(5)	1832(3)	3111(7)
C(6)	5560(5)	2240(3)	4640(7)
C(7)	6736(6)	1788(4)	5795(8)
C(8)	6856(7)	875(4)	5530(8)
C(9)	5841(7)	520(4)	3913(8)
C(10)	4752(6)	935(3)	2735(8)
C(11)	371(5)	2576(6)	2203(7)
C(12)	9830(6)	2152(4)	3482(9)
C(13)	776(6)	1603(4)	4713(8)
C(14)	2263(6)	1476(4)	4696(9)
C(15)	5470(7)	3092(4)	4953(9)
C(16)	6542(7)	3496(4)	6292(9)
C(17)	7736(7)	3047(5)	7391(3)
C(18)	7802(6)	2191(4)	7166(8)
C(19)	2127(6)	3363(3)	−441(7)
C(20)	1575(7)	4116(4)	−20(9)
C(21)	1013(7)	4702(4)	−1360(11)
C(22)	990(7)	4522(5)	−3099(10)
C(23)	1529(8)	3784(5)	−3506(8)
C(24)	2107(7)	3204(4)	−2169(8)
C)25)	3931(6)	540(3)	1013(8)
C(26)	2380(7)	548(4)	327(9)
C(27)	1691(8)	141(5)	−1266(10)
C(28)	2555(8)	−260(4)	−2177(9)
C(29)	4095(9)	−264(5)	−1552(10)
C(30)	4793(11)	133(5)	78(14)

Table 2. Atomic parameters ($\times 10^3$) and isotropic temperature factors of hydrogen atoms

Atom	x	y	z	β/Å
H(9)	602(8)	0(5)	359(10)	4.2(19)
H(11)	−74	263	213	3.7
H(12)	1092	216	348	3.7
H(13)	−30	161	479	3.7
H(14)	296(6)	118(4)	540(8)	1.3(13)
H(15)	460(8)	336(5)	432(10)	3.8(18)
H(16)	639(7)	406(4)	661(9)	3.1(16)
H(17)	852(8)	335(4)	822(10)	4.0(18)
H(18)	876(7)	184(4)	796(9)	3.0(16)
H(20)	158(7)	417(4)	135(9)	2.1(14)
H(21)	44(9)	525(5)	−105(10)	5.0(20)
H(22)	56(7)	495(4)	−412(8)	2.5(16)
H(23)	151(7)	369(4)	−487(9)	2.8(15)
H(24)	253(6)	278(4)	−253(8)	2.5(15)
H(26)	172(7)	82(4)	87(9)	3.2(17)
H(27)	51(7)	15(4)	−174(9)	2.9(17)
H(28)	205(7)	−53(5)	−322(10)	3.9(18)
H(29)	488(8)	−59(5)	−199(10)	5.1(20)
H(30)	585(7)	11(4)	44(9)	3.5(17)

Table 3. Bond lengths and e.s.d.'s of non-hydrogen atoms

Bond length	l/Å	Bond length	l/Å
Br -C(1)	1.871(6)	O -C(8)	1.216(8)
C(1) -C(2)	1.332(8)	C(1) -C(5)	1.532(8)
C(2) -C(3)	1.473(9)	C(2) -C(19)	1.481(7)
C(3) -C(4)	1.400(9)	C(3) -C(11)	1.396(12)
C(4) -C)5)	1.521(8)	C(4) -C(14)	1.385(8)
C(5) -C)6)	1.527(8)	C(5) -C(10)	1.530(8)
C(6) -C(7)	1.399(8)	C)6) -C(15)	1.393(9)
C(7) -C(8)	1.486(9)	C(7) -C(18)	1.391(9)
C(8) -C(9)	1.460(9)	C(9) -C(10)	1.330(9)
C(10)-C(25)	1.490(9)	C(11)-C(12)	1.410(11)
C(12)-C(13)	1.409(9)	C(15)-C(16)	1.380(10)
C(16)-C(17)	1.388(10)	C(17)-C(18)	1.385(10)
C(19)-C(20)	1.383(9)	C(19)-C(24)	1.372(9)
C(20)-C(21)	1.395(11)	C(21)-C(22)	1.388(11)
C(22)-C(23)	1.352(11)	C(23)-C(24)	1.390(10)
C(25)-C(26)	1.369(9)	C(25)-C(30)	1.380(13)
C(26)-C(27)	1.393(10)	C(27)-C(28)	1.363(11)
C(28)-C(29)	1.355(11)	C(29)-C(30)	1.410(14)

Table 4. Bond angles and e.s.d.'s of non-hydrogen atoms

Bond angle	ϕ/°	Bond angle	ϕ/°
Br -C(1) -C(2)	127.0(5)	Br -C(1) -C(5)	119.6(4)
C(2) -C(1) -C(5)	113.3(5)	C(1) -C(2) -C(3)	107.5(5)
C(1) -C(2) -C(19)	128.4(5)	C(3) -C(2) -C(19)	124.2(5)
C(2) -C(3) -C(4)	109.5(6)	C(2) -C(3) -C(11)	130.1(7)
C(4) -C(3) -C(11)	120.2(67)	C(3) -C(4) -C(5)	109.3(5)
C(3) -C(4) -C(14)	121.9(6)	C(5) -C(4) -C(14)	128.8(5)
C(1) -C(5) -C(4)	100.1(5)	C(1) -C(5) -C(6)	109.4(5)
C(1) -C(5) -C(10)	111.3(5)	C(4) -C(5) -C(6)	110.5(6)
C(4) -C(5) -C(10)	111.3(5)	C(6) -C(5) -C(10)	113.4(5)
C(5) -C(6) -C(7)	122.7(5)	C(5) -C(6) -C(15)	119.5(5)
C(7) -C(6) -C(15)	117.8(5)	C(6) -C(7) -C(8)	119.5(5)
C(6) -C(7) -C(18)	120.3(6)	C(8) -C(7) -C(18)	120.2(6)
O -C(8) -C(7)	121.6(6)	O -C(8) -C(9)	121.6(6)
C(7) -C(8) -C(9)	116.8(6)	C(8) -C(9) -C(10)	125.4(6)
C(5) -C(10)-C(9)	120.4(6)	C(5) -C(10)-C(25)	119.2(5)
C(9) -C(10)-C(25)	120.4(6)	C(3) -C(11)-C(12)	117.8(8)
C(11)-C(12)-C(13)	121.2(7)	C(12)-C(13)-C(14)	120.3(6)
C(4) -C(14)-C(13)	118.8(5)	C(6) -C(15)-C(16)	122.0(6)
C(15)-C(16)-C(17)	119.7(7)	C(16)-C(17)-C(18)	119.3(7)
C(7) -C(18)-C(17)	120.8(6)	C(2) -C(19)-C(20)	119.2(5)
C(2) -C(19)-C(24)	121.5(5)	C(20)-C(19)-C(24)	119.4(6)
C(19)-C(20)-C(21)	119.3(6)	C(20)-C(21)-C(22)	120.0(7)
C(21)-C(22)-C(23)	120.5(8)	C(22)-C(23)-C(24)	119.5(7)
C(19)-C(24)-C(23)	121.3(6)	C(10)-C(25)-C(26)	123.8(6)
C(10)-C(25)-C(30)	117.7(7)	C(26)-C(25)-C(30)	118.6(7)
C(25)-C(26)-C(27)	120.4(7)	C(26)-C(27)-C(28)	120.5(7)
C(27)-C(28)-C(29)	120.6(7)	C(28)-C(29)-C(30)	119.1(8)
C(25)-C(30)-C(29)	120.9(9)		

75.80; H, 4.03%.

When a solution of **3c** (5.22 g) in dichloroacetic acid (100 ml) was heated at 120 °C for 1 h and the reaction mixture was worked up as above, **8b** (3.87 g, 90%) was obtained as yellow prisms, mp 189—191 °C; IR 1695 cm^{-1} (C=O); UV 240 (20,500), 295 (13,200), and 360 nm (ε, 9100). Found C, 83.38; H, 4.33%. Calcd for $C_{30}H_{19}OCl$: C,

Table 5. Deviations of the atoms from the least-squares planes

Plane A[a]		Plane B[b]		Plane C[c]		Plane D[d]	
C(2)	−0.002 Å	C(10)	0.015 Å	C(6)	−0.020 Å	C(3)	0.007 Å
C(19)	0.001	C(25)	−0.009	C(7)	0.004	C(4)	−0.009
C(20)	−0.003	C(26)	−0.016	C(15)	0.016	C(11)	−0.002
C(21)	0.005	C(27)	0.064	C(16)	0.004	C(12)	−0.000
C(22)	−0.004	C(28)	0.014	C(17)	−0.021	C(13)	−0.002
C(23)	−0.001	C(29)	−0.008	C(18)	0.017	C(14)	0.007
C(24)	0.004	C(30)	−0.003	C(8)[e]	−0.006	H(14)[e]	0.040
H(20)[e]	−0.061	H(26)[e]	−0.033	O[e]	0.103	C(2)[e]	−0.078
H(21)[e]	−0.140	H(27)[c]	0.014	C(9)[e]	−0.224	C(1)[e]	−0.158
H(22)[e]	−0.012	H(28)[e]	0.047	C(10)[e]	−0.313	C(5)[e]	−0.037
H(23)[e]	0.025	H(29)[e]	0.113	C(25)[e]	−0.723	Br[e]	−0.330
H(24)[e]	0.113	H(30)[e]	−0.011	C(5)[e]	−0.037	C(19)[e]	−0.042
				H(15)[e]	0.155		
				H(16)[e]	0.160		
				H(17)[e]	−0.126		
				H(18)[e]	−0.059		

The equation of plane is: $0.9017X+0.3990Y-0.0920Z-3.930=0$. b) The equation of plane is: $-0.2029X-0.8477Y+0.5273Z+1.035=0$. c) The equation of plane is: $-0.7690X-0.1649Y+0.8078Z+1.541=0$. d) The equation of plane is: $0.1259X+0.7591Y+0.5781Z-4.176=0$. e) Omitted from the least-squares plane calculation.

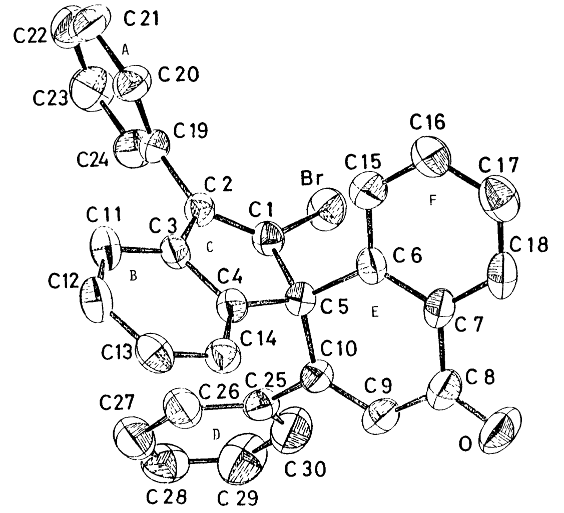


Fig. 1. Perspective view of **13** and the crystallographic numbering of carbon atoms.

83.62; H, 4.41%.

*Synthesis of 7,8,8-Tribromo-2,5,5-triphenyl-3,4-benzobicyclo[4.2.0]octa-1,3,6-triene (**5**).* A solution of **3b** (1.36 g) in benzene (35 ml) containing a small amount of conc H_2SO_4 was heated under reflux for 7 h. The crude product remained after evaporation of the solvent was recrystallized from acetone to give **5** (0.53 g, 44%) as colorless prisms, mp 159—160 °C; UV 326 (12,600) and 252 nm (ε, 21,400); MS (*m/e*) 622, 620, 618, and 616 (M^+). Found: C, 58.47; H, 2.86%. Calcd for $C_{30}H_{19}Br_3$: C, 58.19; H, 3.07%.

*Synthesis of 7,8-Dibromo-5-methoxy-2,5,6-triphenyl-3,4-benzobicyclo[4.2.0]octa-1,3,7-triene (**6b**).* A solution of **5** (0.4 g) in THF-MeOH (3:1, 20 ml) was treated with $AgClO_4$ (0.4 g) at room temperature. Excess $AgClO_4$ was decomposed with NaCl and filtered. The crude product remained after evaporation of the solvent of the organic layer was extracted with ether. The ether solution was washed with water and dried over Na_2SO_4. Crystals obtained from the ether solution were recrystallized from acetone–$CHCl_3$ (1:1) to give **6b** (0.3 g, 81%) as colorless prisms, mp 215—216.5 °C; IR 1075 cm^{-1} (ether); ^{1}H NMR δ 2.79 (s, MeO) and 6.3—7.8 (m, Ph). Found: C, 65.21; H, 3.81%. Calcd for $C_{31}H_{22}OBr$: C, 65.26; H, 3.86%.

*Thermal Reaction of **5** and **6b** in Dichloroacetic Acid.* A solution of **5** (3.1 g) in dichloroacetic acid (50 ml) was heated at 120 °C for 1 h. The reaction mixture was worked up as done for the thermal reaction mixture of **3b** in dichloroacetic acid, and **8a** (0.76 g, 32%) and **13** (0.83 g, 35%) were obtained. When **6b** (0.1 g) was heated in dichloroacetic acid (10 ml) at 120 °C for 30 min and then worked up as above, **8a** (0.075 g, 88%) was obtained.

*Potassium Permanganate Oxidation of **8a**.* When $KMnO_4$ (0.5 g) was added to a solution of **8a** (0.1 g) in acetone (10 ml), exothermic reaction occurred. After 3 h, excess $KMnO_4$ was decomposed with MeOH, and MnO_2 was filtered. Crude product remained after the evaporation of the solvent of acetone solution was recrystallized from acetone to give **17** (0.55 g, 60%) as colorless prisms, mp 244—245 °C (lit,[4] 245 °C). IR spectrum was identical to that of the authentic sample.[4]

*Base-catalyzed Addition of MeOH to **8a**.* A solution of **2** (1.0 g) in THF (10 ml) was added to 5% KOH-MeOH (30 ml) and then heated under reflux for 1 h. Crude product remained after the evaporation of the solvent was washed with water, dried, and recrystallized from ethyl acetate to afford **18a** (0.95 g, 84%) as pale yellow prisms, mp 215—217 °C; IR 1710 cm^{-1} (C=O); UV 288 (18,600) and 358 nm (ε, 900); ^{1}H NMR δ 2.98 (s, MeO), 3.57 (s, CH), and 6.5—7.5 (m, Ph); MS (*m/e*) 508 and 506 (M^+). Found: C, 73.10; H, 4.35%. Calcd for $C_{31}H_{23}O_2Br$: C, 73.38; H, 4.54%.

*$AlCl_3$-catalyzed Addition of Benzene to **8a**.* A mixture of **8a** (1.0 g), benzene (20 ml), and $AlCl_3$ (1.0 g) was stirred at room temperature for 3 h. The reaction mixture was decomposed with water and extracted with benzene. The benzene solution was washed with dil HCl and water, and dried over Na_2SO_4. Crude crystals obtained by the evaporation of the solvent were recrystallized from ethyl acetate to give **18b** (1.05 g, 90%) as colorless prisms, mp 255 °C; IR 1710 cm^{-1} (C=O); UV 215 (43,300) and 285 nm (ε,

8500); ^{1}H NMR δ 4.2 (s, CH) and 6.6—7.6 (m Ph); MS (*m/e*) 554 and 552 (M^+). Found: C, 77.82; H, 4.39%. Calcd for $C_{36}H_{25}OBr$: C, 77.93; H, 4.52%.

*X-Ray Analysis of **13**.* A crystal used for the intensity measurement was $0.3 \times 0.2 \times 0.2$ mm^3. Intensity data were obtained on a Rigaku four-circle automatic diffractometer, equipped with graphite-monochromated Cu $K\alpha$ radiation, and using the $2\theta/\omega$ scan technique ($2\theta \leqq 130°$). Two thousands sixty one independent reflections of $F_o \geqq 3\sigma(F_o)$ were corrected for Lorentz and polarization factors but not for absorption.

Crystal data: $C_{30}H_{19}OBr$, monoclinic, $P2_1$, $Z=2$, $a=9.139(2)$, $b=16.020(3)$, $c=7.838(4)$ Å, $\beta=106.2(1)°$, $D_c=1.433$ g cm^{-3}, $\mu=3.2$ mm^{-1} (for Cu $K\alpha$)

The structure was solved by the heavy atom method. The positions of hydrogen atoms were located from the difference Fourier map. The positional and thermal parameters were refined by the block-diagonal least-squares method. The R factor was converged to 0.034 with an equal weight for each reflection.

We thank Professor H. H. R. Hoffmann of Technischen Universität at Hannover for sending IR spectrum of **17** (Ref. 4) which had been recorded by Professor G. Köbrich at the same University.

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