by this method. All of structures were determined by comparison with commercially available authentic samples of **6**, and the isomeric purity was confirmed by GLC.

6f: yellow oil; MS, m/e (M^+) calcd for $C_8H_9NO_2$ 151.0634, obsd 151.0647.

6g: yellow oil; MS, m/e (M^+) calcd for $C_7H_7NO_2$ 137.0477, obsd 137.0501.

6h: mp 49–50 °C (lit.[22] mp 54.4 °C); MS, m/e (M^+) calcd for $C_7H_7NO_2$ 137.0477, obsd 137.0507.

Reaction of 2 with 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene. A mixture of **2** (0.94 g, 4.77 mmol) and the diene (1.12 g, 6.51 mmol) in toluene was heated at 110 °C for 3 h. The reaction mixture was subjected to column chromatography (silica gel/hexane–ethyl acetate) to give *p*-nitrophenol (0.34 g, 51%): mp 113–115 °C (lit.[23] mp 114 °C); NMR δ ($CDCl_3$) 8.20 (d, J = 8 Hz, 2 H), 7.00 (d, J = 8 Hz, 2 H), 6.85–6.70 (m, 1 H).

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Registry No. **1a**, 101933-29-3; **1b**, 101933-39-5; **1c**, 101933-45-3; **2**, 101933-28-2; **3a-A**, 101933-49-7; **3a-B**, 102043-92-5; **3b-A**, 106185-49-3; **3b-B**, 106248-46-8; **3c-A**, 106185-50-6; **3c-B**, 106248-47-9; **3d**, 106185-52-8; **3e**, 111905-19-2; **3f-A**, 111957-34-7; **3f-B**, 111957-35-8; **3g-A**, 101933-51-1; **3g-B**, 102043-93-6; **3h-A**, 111905-20-5; **3h-B**, 111957-36-9; **3i-A**, 111905-21-6; **3i-B**, 111957-37-0; **3j-A**, 111905-22-7; **3j-B**, 111905-23-8; **3k-A**, 111905-24-9; **3k-B**, 111905-25-0; **3l**, 106185-54-0; **3m-A**, 111957-38-1; **3m-B**, 111957-39-2; **3m-A**, 111905-26-1; **3n-B**, 111957-40-5; **3o-A**, 111905-27-2; **3o-B**, 111905-28-3; **3p**, 106185-57-3; **4a**, 2734-13-6; **4b**, 111905-29-4; **4c**, 38116-47-1; **4d**, 111905-30-7; **4e**, 111905-31-8; **4f**, 106185-58-4; **5a**, 101933-50-0; **5a'**, 111905-33-0; **5c**, 111905-34-1; **5c'**, 111905-35-2; **5d**, 111905-36-3; **6a**, 88-72-2; **6a'**, 99-08-1; **6b**, 86-00-0; **6b'**, 2113-58-8; **6c**, 99-99-0; **6c**, 99-51-4; **6e**, 98-95-3; **6f**, 7369-50-8; **6f'**, 612-22-6; CH_2=CHCH=CH_2, 106-99-0; (*E*)-TMSOCH=CHCH=CH_2, 63383-46-0; (*E*)-CH_2=CHCH=CHMe, 2004-70-8; (*E*)-CH_2=CHCH=CHC_7H_{15}, 79309-74-3; (*E,E*)-PhCH=CHCH=CHPh, 538-81-8; CH_2=C(Me)CH=CH_2, 78-79-5; $(Me)_2C$=$CH(CH_2)_2C$(=CH_2)CH=CH_2, 123-35-3; MeC(=CH_2)C(=CH_2)Me, 513-81-5; (*E*)-CH_2=CHCH=CHPh, 16939-57-4; (*E*)-CH_2=CHCH=CHOAc, 35694-20-3; (*E*)-CH_2=CHC(Et)=CHOAc, 111905-32-9; (*E,E*)-EtCH=CHCH=CHOAc, 91438-29-8; (*E*)-CH_2=CHC(Me)=CHOAc, 86400-08-0; (*E*)-CH_2=C(Me)CH=CHOAc, 52062-24-5; (*E*)-TMSOC(=CH_2)CH=CHOMe, 54125-02-9; *p*-$NO_2C_6H_4OH$, 100-02-7; cyclopentadiene, 542-92-7; furan, 110-00-9; cyclohexadiene, 592-57-4; anthracene, 120-12-7.

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Diisophorone and Related Compounds. 21.[1] Synthesis and Nucleophilic Reactions of 4,4,8- and 4,6,8-Tribromodiisophorones

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Halogenation of diisophorone (**1**) by 3 mol of bromine in acetic acid yields the 4,4,8-tribromo 3-ket-1-ol **2**, which is converted by Koch–Haaf carboxylation into the 4,4,8-tribromo 1-carboxylic acid **8**. The latter undergoes ring A contraction (to **10**) or ring A aromatization (to **11**) by the action of alkali or alkoxide, respectively. In contrast, tribromination in ether converts the parent ketol **1** predominantly into the 4,6,8-tribromo derivative **14**, which is also accessible unequivocally from the 4-mono and 4,8-dibromo analogues by the action of *N*-bromosuccinimide. Its interaction with nucleophiles proceeds by ring A aromatization, yielding 8-substituted 4-bromo-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diols **19–22**. The structural assignments are in accord with the spectral properties of the new types of compounds, especially their carbon NMR and mass spectra.

Introduction

The controlled introduction of halogen substituents into the diisophorone structure provides reactive centers suitable for the investigation of further reactions at specific positions in this three-dimensional ring system. Both 4-[2] and 8-monobromo-[3-5] as well as 4,8-[6,7] and 6,8-dibromodiisophorones,[8] obtained by appropriate halogenation procedures, have been studied from this point of view. Their reactions with nucleophiles may involve simple replacements, with[5,6,9,10] or without[2,6] isomerization, or ring A contraction,[7] or ring A aromatization,[8,11] the preferred course depending on the number and position of the halogen substituents. We now close our account of this group of reactions with a report of the synthesis and behavior toward nucleophiles of 4,4,8- and 4,6,8-tribromodiisophorones, and with an attempt to correlate the sum of the available information.

The compounds now described are derivatives of tricyclo[7.3.1.$0^{2,7}$]tridecane, except **10**, which is a substituted tricyclo[6.3.1.$0^{2,6}$]dodecane. We continue to employ the simplified nomenclature and numbering that was originally

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Table I. Resonances of Diisophorone Carbon Atoms at and Adjacent to Bromination Sites[a]

	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-13
diisophorone[13] (1)	200.7 s	51.8 t	32.2 s	45.7 t	157.5 s	46.6 t	32.4 s	46.6 t
8-bromo[13]	202.1 s	52.2 t	32.6 s	44.0 t	**153.0** s	65.9 d	**37.2** s	**39.3** t
4-bromo[2] (13)	**193.2** s	63.6 d	**37.1** s	45.5 t	157.0 s	42.5 t	32.3 s	46.3 t
4,8-dibromo[6] (5)	**194.5** s	62.0 d	**36.6** s	40.0 t	**153.3** s	65.1 d	**36.1** s	**37.9** t
4,4,8-tribromo (2)	**186.7** s	83.0 s	**45.0** s	43.3 t	**152.6** s	64.1 d	**36.3** s	**37.5** t
6,8-dibromo[8]	200.4 s	45.0 t	**35.7** s	61.4 d	**149.4** s	63.3 d	**36.5** s	**36.3** t
4,6,8-tribromo (14)	**192.6** s	62.3 d	**42.5** s	61.0 d	**149.3** s	63.1 d	**35.7** s	**36.4** t

[a] Numbers in bold type emphasize the changes in chemical shift of the carbon atoms adjacent or proximate to the bromination sites at C-4, 6, and 8.

adopted[12] for diisophorones and subsequently extended to the related ring A aromatized[11] and ring A contracted[7] structures.

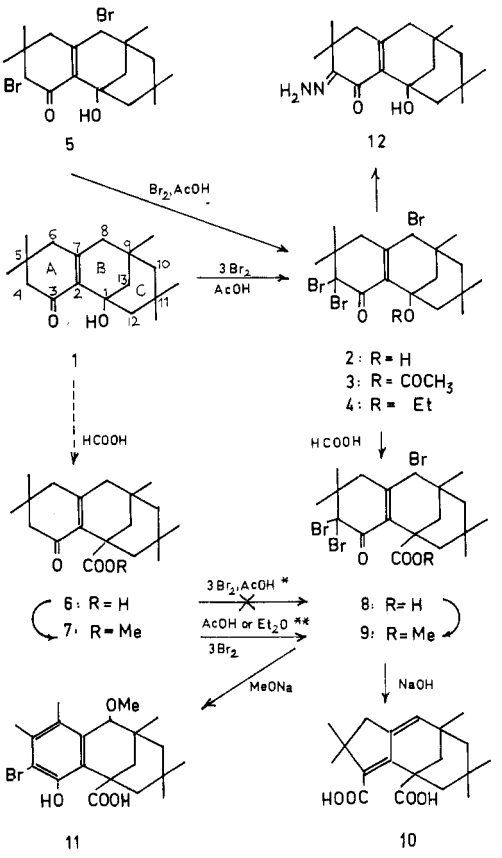
Results and Discussion

Molecular bromine in glacial acetic acid converts diisophorone (1) as well as its 1-carboxy analogue **6** successively into the 8-mono[3-5] and 4,8-dibromo derivatives.[6,7] Continued bromination occurs by a less precisely defined substitution pattern, but may under appropriate conditions be channelled into almost exclusive production of the 4,4,8- or predominant formation of the 4,6,8-tribromo compounds, in both the 3-ket-1-ol and 1-carboxylic acid series.

4,4,8-Tribromodiisophorones. The action of 3 mol of bromine in *glacial acetic acid* converted diisophorone (1) into 4,4,8-tribromodiisophor-2(7)-en-1-ol-3-one (2) in good yield. The location of the halogen substituents, suggested by the alternative formation of **2** by monobromination of the authentic 4,8-dibromo analogue[6] (**5** → **2**), is confirmed by the carbon NMR spectral evidence. The carbon atom of the *gem*-dibromo moiety produces in each example (**2**, **3**, **9**) a new singlet (at ca. 84 ppm; see Table II), replacing the familiar C-4 triplet of the parent ketol (**1**)[13] or the C-4 doublet of the 4-mono (**13**)[2] or 4,8-dibromo analogue (**5**).[6] That the 4- rather than the 8-position is the site of the *gem*-dibromo grouping is shown by the data presented in Table I. The progressive change from the parent ketol 1 via the 4-monobromo (**13**) to the 4,4,8-tribromo compound (**2**) is attended by a stepwise displacement in the chemical shifts of the 3-keto carbon and the quaternary C-5 carbon, both adjacent to C-4. In contrast, the chemical shifts of C-7 and C-9 (adjoining C-8) and of the sterically proximate C-13 carbon are near-identical in the 8-mono-, 4,8-di-, and 4,4,8-tribromo analogues, in accord with the same degree of substitution at C-8 in each of these structures. The occasional appearance of the 4,6,8-tribromo isomer **14** as a minor byproduct in the production of **2** is discussed below.

The 1-ethoxy homologue of diisophorone[14] similarly yielded a 4,4,8-tribromo derivative (**4**), but the attempted analogous tribromination of the diisophorone-1-carboxylic acid (**6**) terminated consistently with the formation of the known[6] 4,8-*di*bromo compound (Scheme I). Similarly, the methyl ester **7** gave the 4,8-*di*bromo ester as the major product (56%) and only small proportions of the expected 4,4,8-tribromo derivative **9** (18%); the same two products arose in approximately equal yield (20–30%) in diethyl ether. No plausible explanation of these anomalies can at present be proposed. The desired 4,4,8-tribromo 1-carboxylic acid **8** was readily accessible, however, by Koch–Haaf carboxylation[15] of the 4,4,8-tribromo ketol **2**.

Scheme I[a]



[a] Key: *, this reaction yields the 4,8-dibromo 1-carboxylic acid; **, for the proportions of 4,4,8-tri- and 4,8-dibromo ester (main product), see Experimental Section.

The -CBr_2- moiety thus shares with the -CHBr- grouping in cyclohexane the high stability toward severe acidic conditions already seen in the 4-[2] and 8-mono-[5] and 4,8-[6] and 6,8-dibromodiisophorones.[8]

4,6,8-Tribromodiisophorones. The action of bromine (3.75 mol) in ether has been reported[4] to convert the parent β-ketol 1 into the 4,6,8-tribromo compound **14** in high yield (Scheme II). The reaction produces in fact both the 4,4,8- and 4,6,8-tribromo isomers **2** and **14** in proportions depending on the experimental conditions: The former (**2**) is the sole product of the slow halogenation in dilute solution (up to 45%), while the latter (**14**) arises preferentially (45–50%) but not exclusively by more rapid action at higher concentration.

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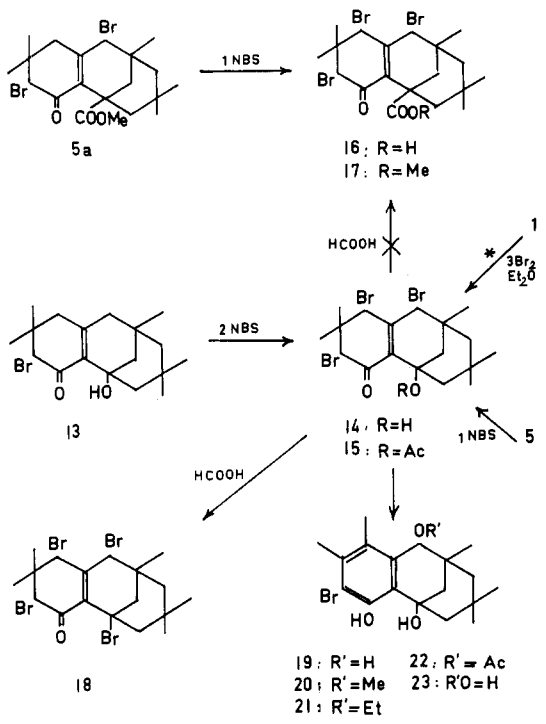
Scheme II[a]



[a] Key: *, the reaction yields appreciable proportions of the 4,4,8-tribromo isomer **2**.

The location assigned to the substituents in the 4,6,8-tribromo isomer **14** is consistent with its unequivocal synthesis by homolytic bromination of authentic 4-bromo-(**13**)[12] or 4,8-dibromodiisophor-2(7)-en-1-ol-3-one (**5**)[6] with *N*-bromosuccinimide (2 or 1 mol, respectively), the attack of which at the allylic 6- and 8-positions of diisophorone is established.[3,4,8] The carbon NMR spectrum of **14** (Table I) displays three doublets, the chemical shifts of which match those of the halogen-bearing carbon atoms in the 4-mono- and 4,6- and 4,8-dibromo analogues. Moreover, displacements of the signals of the carbons flanking the 4-, 6-, and 8-positions (of **14**) agree closely with those occurring in these reference compounds (Table I).

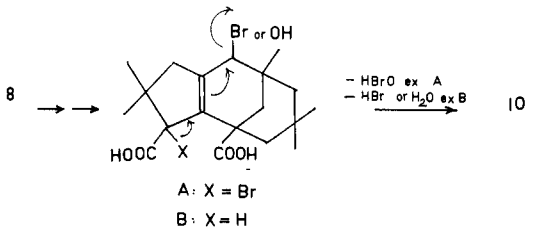
In attempts to convert the 4,6,8-tribromo ketol **14** into the corresponding 1-carboxylic acid **16** by the Koch–Haaf reaction,[15] the main product was unexpectedly the 1,4,6,8-tetrabromo compound **18**. One of the normally firmly held bromine substituents (of **14**) appears to become detached as hydrogen bromide, which effects the 1-hydroxy bridgehead replacement in a manner comparable with that occurring in the remarkably ready conversion of the parent ketol **1** into 1-chlorodiisophor-2(7)-en-3-one by concentrated hydrochloric acid.[3] Although the desired carboxylation (**14** → **16**) did occur to some extent, concomitant dehalogenation led to nonuniform products. Allylic bromination was suitable for producing the 4,6,8-tribromo ester **17** from its 4,8-dibromo analogue **5a**,[6] but was inapplicable to the free acid **16** because of the low solubility of the precursor 4,8-dibromo 1-carboxylic acid in suitable solvents.

The divergent course of the bromination of diisophorone (**1**) under different conditions now and previously[5–8] observed may reasonably be ascribed to the operation of alternative mechanisms. Homolytic attack by bromine radicals arising from *N*-bromosuccinimide clearly accounts for the successive halogenation at the allylic C-8 and C-6 positions. The lower reactivity of the latter may be traced to the effect of the adjacent 5,5-dimethyl group. Similarly, the demonstrated[8] resistance of the 4-methylene position (of **1**) to free-radical bromination, a reaction that does occur in cyclohexanone,[16] is probably due to the same cause.

In contrast, the channelling of three halogen substituents successively into the C-8 and two C-4 positions by bromine in acetic acid (resulting in **2**) is thought to occur by an electrophilic attack by brominium cations (joined to a suitable "carrier"[17]) on the transiently enolized[18] reactant. The comparable α,α-dihalogenation of ketones, both by molecular bromine[19–21] and *N*-bromosuccinimide,[22] is a well-known reaction, especially of steroids: the introduction of the first electronegative substituent next to the carbonyl group facilitates the release of the remaining α-proton and promotes further substitution at this site.[20] The preferential formation of the 4,6,8-tribromo compound **14** in ether, however, reflects the predominant generation and function of free radicals in this solvent. Finally, the operation of the two mechanisms accounts for the general observation that none of the bromination procedures yield entirely uniform products.

Nucleophilic Reactions. The present tribromodiisophorones display the high reactivity toward nucleophiles already encountered and elucidated in the mono-[2,5,9–11] and dibrominated[6–8] series of compounds.

4,4,8-Tribromo Series. The action of alkali on 4,4,8-tribromodiisophor-2(7)-ene-1-carboxylic acid (**8**) resembles closely that of its 4,8-dibromo analogue[7] in producing excellent yields of the same tricyclo[6.3.1.$0^{2,6}$]dodecanedicarboxylic acid **10** by a ring A contraction of the Favorski type. The reaction is therefore explicable in terms of the



usual semibenzilic mechanism,[7] except for the removal of the 4-bromo substituent instead of a 4-proton from the respective penultimate intermediates (A or B, participating as 8-bromo or more likely 8-hydroxy species); its disposal as hypobromite by the alkaline medium would meet this requirement (see Scheme I).

According to precedent,[7] methanolysis of the 4,4,8-tribromo 1-carboxylic acid **8** should yield the 3-methoxycarbonyl homologue of **10**; the reaction occurred in fact with ring A aromatization, producing moderate yield (33–40%) of the benzenoid 2(7),3,5-triene **11**. Its probable mechanism is comparable with that of the aromatization of the 4,6,8-tribromo compounds (see Scheme III), but no satisfactory explanation for the diverging course of the alkaline hydrolysis and methanolysis (of **8**) can at present be suggested.

The action of alkali *or* sodium alkoxides on the 4,4,8-tribromo ketol **2**, causing rapid resinification, failed to yield

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Table II. Carbon NMR Spectra of Diisophorones and Their Assignments

compd[a]	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
					4,4,8-Tribromodiisophorones						
2	71.9 s	132.2 s	186.7 s	83.0 s	45.0 s	37.5 t	152.6 s	64.1 d	36.3 s	49.0 t	31.6 s
3	78.8 s	131.1 s	182.4 s	84.7 s	44.9 s	35.0 t	149.6 s	63.8 d	36.7 s	47.4 t	31.2 s
4	77.2 s	132.8 s	182.0 s	84.3 s	44.8 s	33.9 t	153.0 s	64.8 d	36.2 s	*47.0 t	31.4 s
9	*45.6 s	131.8 s	183.5 s	82.8 s	*45.2 s	34.5 t	151.0 s	63.6 d	34.4 s	46.8 t	30.1 s
					4,6,8-Tribromodiisophorones						
14	72.0 s	135.4 s	192.6 s	+62.3 d	42.5 s	+61.0 d	149.3 s	63.1 d	35.7 s	49.5 t	31.5 s
15	78.9 s	135.0 s	187.9 s	+61.8 d	42.2 s	+61.8 d	146.8 s	63.6 d	36.0 s	45.7 t	31.1 s
17	45.7 s	134.6 s	189.9 s	+56.6 d	38.8 s	+56.1 d	148.2 s	62.5 d	34.2 s	45.6 t	30.0 s
18	57.7 s	136.2 s	188.3 s	+60.6 d	41.1 s	+59.8 d	147.6 s	61.4 d	37.3 s	51.0 t	33.1 s
					Substituted 6-Methyl-5-nordiisophora-2(7),3,5-trienes						
19	74.9 s	*126.6 s	151.8 s	114.0 s	+136.8 s	*128.0 s	+138.7 s	72.9 d	39.1 s	°50.4 t	31.3 s
20	74.5 s	*127.4 s	151.8 s	114.6 s	+135.8 s	*128.1 s	+136.7 s	82.5 d	39.8 s	°50.2 t	31.1 s
21	75.4 s	*125.7 s	149.9 s	114.8 s	+135.0 s	*128.4 s	+137.2 s	81.4 d	39.5 s	°49.7 t	31.2 s
22	74.4 s	*127.6 s	152.0 s	115.6 s	+133.9 s	*127.8 s	+137.3 s	74.8 d	38.6 s	°49.9 t	31.1 s
11	46.6 s	*130.0 s	146.9 s	114.6 s	+135.5 s	*125.8 s	+135.6 s	82.0 d	37.0 s	49.4 t	29.6 s

compd[a]	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22
					4,4,8-Tribromodiisophorones						
2	47.5 t	43.3 t	*22.9 q[b]	*27.3 q[b]	32.0 q	32.8 q	35.4 q				
3	45.0 t	43.2 t	*22.4 q[b]	*27.6 q[b]	31.9 q	33.0 q	35.5 q	170.1 s	21.7 q		
4	*46.8 t	44.3 t	25.4 q[b]	25.4 q[b]	31.4 q	33.6 q	35.0 q	58.5 t	16.0 q		
9	43.1 t	40.0 t	*21.8 q[b]	*27.6 q[b]	31.4 q	33.7 q	34.7 q	175.6 s	52.2 q		
					4,6,8-Tribromodiisophorones						
14	45.3 t	36.4 t	*29.9 q	*20.9 q	31.3 q	33.9 q	34.6 q				
15	44.9 t	33.7 t	*30.4 q	*21.6 q	31.1 q	34.3 q	34.5 q	170.2 s	20.6 q		
17	40.7 t	34.3 t	*27.5 q	*26.6 q	31.1 q	34.4 q	34.6 q	175.5 s	52.3 q		
18	*44.7 t	*44.2 t	°28.7 q	°22.2 q	31.2 q	33.1 q	35.3 q				
					Substituted 6-Methyl-5-nordiisophora-2(7),3,5-trienes						
19	°50.1 t	42.1 t	20.5 q	16.1 q	*29.0 q	*29.3 q	37.7 q				
20	°49.9 t	42.9 t	20.7 q	16.9 q	*29.1 q	*29.2 q	37.6 q			58.7 q	
21	°48.9 t	42.5 t	20.7 q	16.8 q	*29.1 q	*29.0 q	37.3 q			66.2 t	15.9 q
22	°49.4 t	42.9 t	+20.6 q	16.1 q	*28.4 q	*28.8 q	37.5 q			170.1 s	20.8 q
11	42.3 t	38.3 t	20.7 q	16.4 q	28.8 q	30.3 q	37.3 q	182.9 s		58.6 q	

[a] Spectra were determined in deuteriochloroform except for the sparingly soluble **19**, **20**, and **22**, where deuteriopyridine was used. [b] Broad low-intensity signal. [c] *, +, and °: for each compound like signals may be interchanged.

identifiable products. Hydrazinolysis gave moderate yields (40%) of 4-hydrazonodiisophor-2(7)-en-1-ol-3-one (**12**); the same reaction is undergone more effectively by the 4-[2] or 8-mono-[9] (50-64%) or 4,8-dibromo ketol (75–80%).[6]

4,6,8-Tribromo Series. The action of nucleophiles on 4,6,8-tribromodiisophorone (**14**) presents a more consistent pattern in that it results invariably in ring A aromatization. Thus, alkaline hydrolysis, alcoholysis or base-catalyzed acetolysis converted the reactant into the appropriately 8-substituted 4-bromo-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diols **19–22** in high yield. Except for the retention of the 4-bromo substituent the reactions are identical with those of the 6,8-dibromo analogues.[8] Scheme III outlines a unifying mechanism for the ring A aromatization in 6,8-dibromo- and 4,6,8- and 4,4,8-tribromodiisophorones, all terminating in structures of type F. Its essential features are the enolation of the 3-keto function, migration of one of the 5-methyl groups by a Wagner–Meerwein rearrangement, and introduction of a double bond by a net dehydrobromination. The obvious scope for minor variations in the direction of enolization and sequence of the stages is understood. It would appear that aromatization is favored more especially by the participation of the 6-bromo substituent, the elimination of which leads most directly to the creation of the aromatic structure.

The solvolysis of 4,6,8-tribromodiisophorone (**14**) by aqueous ethanolic potassium carbonate has been reported by Morizur et al.[4] to yield a mixture (separable chromatographically) of the direct 6-substitution product (i.e., the 4,8-dibromo 1,6-diol, 12%) together with the aromatized compounds **19** (20%) and **21** (16%). The difficulty of their complete separation is probably the reason for the minor discrepancies in their reported physical constants and those of the authentic compounds **19** and **21** now separately obtained in the individual reactions. Our previous surmise[11] that Morizur's compounds may be 4,5-dimethyl isomers of **19** and **21**, occasioned by the apparent nonidentity of their hydrogenolysis product **23** with authentic material,[23] is therefore not sustained: 5,6-dimethyl compounds are the products of all the present comparable reactions.

Spectral Data. ^{13}C NMR Spectra. The carbon NMR spectra of both series of tribromodiisophorones and their aromatized products are displayed in Table II in accordance with their proposed assignments. The individual signals were generally readily identified by reference to the fully mapped spectra of several series of diisophorone derivatives.[8,13,24] The detailed reasoning leading to the interpretation of these model spectra is on record, and, being ultimately applicable to the present examples, is now omitted. The spectral data are self-consistent and compatible with the proposed structures and contribute in some instances independently to the structural evidence. Brief comments on the new numerical results and their attributions appear in the supplementary material section of this paper.

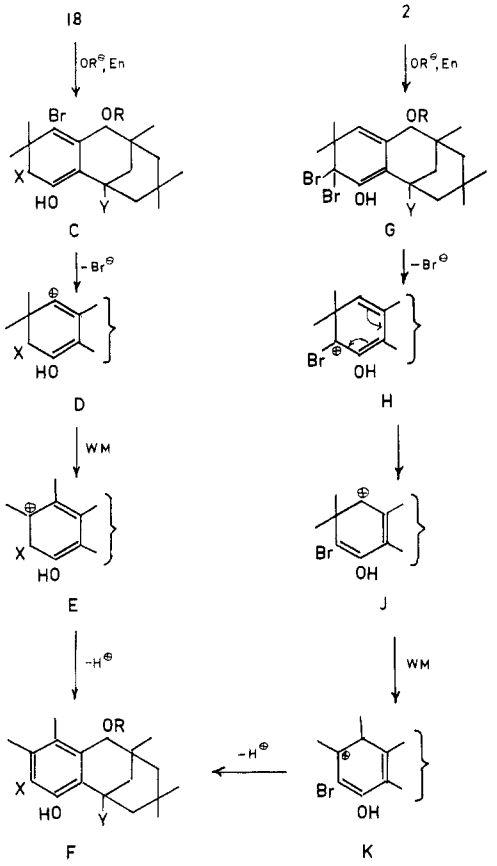
Mass Spectra. The scission under electron impact of diisophorone β-ketols,[25] 1-carboxylic acids,[6] as well as ring A aromatized[8] and ring A contracted examples[7] has previously been elucidated and discussed. The present tri-

(23) The misinterpretation was compounded by the disagreement in the physical characteristics of **23** given in the Discussion and Experimental Section of Morizur's paper[4] (mp 207–209 °C and 192–194 °C, the former approaching that of authentic **23**[11]).

(24) Kurzer, F.; Patel, J. N. *Monatsh. Chem.* **1984**, *115*, 825.

(25) Kossanyi, J.; Morizur, J. P.; Furth, B.; Vandewalle, M. *Bull. Soc. Chim. Fr.* **1967**, 2180.

Scheme III[a]



[a] En = enolization. WM = Wagner–Meerwein rearrangement. X = Br in 4,6,8-tribromo; X = H in 6,8-dibromodiisophorones.

brominated diisophorones produce comparable fragmentation patterns, indicating the successive loss of the peripheral substituents and removal of ring C by elimination of the neopentyl radical ($^{\bullet}CH_2CMe_3$, m/e 71) or of isopropylidene ($CH_2{=}CMe_2$, m/e 56), leading to the appropriate ionic fragments having the usual[25] naphthalene or tropylium structure.

The characteristic features of the scission of the partly aromatized compounds (**11**, **19–22**) include the early loss of the elements of water (involving presumably the 1- and 3-hydroxy groups) and stepwise removal of all the substituents, leading to a common fragment ($C_{18}H_{22}$, m/e 238) in all the examples. The 4-bromo substituent is attached more firmly to the aromatic ring A than to cyclohexane moieties of the diisophorone structure, as shown by its retention in prominent fragmentation intermediates. The usual detachment of ring C by two modes of fission is again observed. Schemes for the fragmentations may readily be constructed from the individual numerical data (see Experimental Section); they follow closely the previously proposed patterns[6,8,25] and are therefore not detailed.

Conclusion

It seems significant that all the reactions of diisophorone so far encountered occur at sites of its near-planar ring A/B system. Although ring C, forming a bicyclo[3.3.1]nonane framework with ring B, should in principle not be devoid of reactivity,[26] it displays once again total inertness in the present multistage bromination. It may be that the "folded" location of ring C below rings A/B, coupled with a low probability of lateral reagent approach toward the external face of ring C, contributes to the observed inactivity of this region of the molecule.

(26) Buchanan, G. L. In *Topics in Carbocyclic Chemistry*; Lloyd, D., Ed.; Logos Press: London, 1969; Vol. 1, p 199.

Experimental Section

The equipment used in the determination of the spectral data, information concerning general methods, reagents, and solvents, and abbreviations are as specified in previous papers of this series,[2,12] especially in the immediately preceding paper.[1]

The identity of compounds from different sources was in all cases confirmed by mixture melting point determination and comparison of IR spectra and is not separately mentioned. Full spectral data are given for the four representative compounds **2**, **8**, **14**, and **19**; in the case of their structural analogues, this information is provided in the supplementary material section.

4,4,8-Tribromo Compounds. 4,4,8-Tribromodiisophor-2(7)-en-1-ol-3-one (2) (IUPAC name: 3,3,10-Tribromo-5-hydroxy-2,2,7,7,9-pentamethyl-2,3,5,6,7,8,9,10-octahydro-5,9-methanobenzocycloocten-4(1*H*)-one). (a) A stirred solution of diisophorone (**1**; 9.1 g, 33 mmol) in glacial CH_3COOH (160 mL) –60% HBr (0.5 mL) was treated dropwise at room temperature with 1 M bromine in glacial CH_3COOH (100 mL, 100 mmol) during 3 h. The pale-orange liquid was stirred for another 30 min and then added to ice–water (500 mL). The yellow resinous material was transferred to fresh H_2O, thoroughly rinsed, air-dried, and dissolved in light petroleum ether (bp 40–60 °C, 3 × 25 mL). The liquid deposited successive crops of prisms, the first two of which (mp 85–90 °C; 7.6–9.3 g, 45–55%) gave prisms of **2**, mp 86–89 °C (from the same solvent). UV: λ_{max} 213 nm (log ϵ 3.79); 272 (3.78). IR: 3550 vs (OH), 2970 vs–2870 s, 1475 s, 1415 s (CH_3, CH_2), 1670 vs (CO), 1630 s (C=C conjug), 1375 s, 1210 ms, 1130 m, 1110 m, 1080 m, 1050 s, 1005 m, 960 mw, 910 mw, 880 m, 810 mw, 725 s, 685 ms cm^{-1}. MS, m/e: 516, 514, 512, 510 vvw ($M^{+\bullet}$), 499, 497, 495, 493 vw (M – 17, OH), 445, 443, 441, 439 vs max (M – 71, C_5H_{11}), 435, 433, 431 ms (M – Br), 417, 415, 413 m (M – Br – 17 – 1), 379, 377, 375 m (M – Br – 56, C_4H_8), 364, 362, 360 s (M – Br – 71), 354, 352 s (M – 2Br), 298, 296 s (M – 2Br – 56), 283, 281 s (M – 2Br – 71), 282, 280 ms (M – 2Br – 71 – 1), 273 w (M – 3Br), 202 s (M – 3Br – 71), 201 s (M – 3Br – 71 – 1 or M – 3Br – 56 – 17 + 1); 393, 391, 389 s; 313, 311 vs; 312, 310 vs; 188 ms, 187 ms. Anal. Calcd for $C_{18}H_{25}Br_3O$: C, 42.1; H, 4.9; Br, 46.75. Found: C, 42.7; H, 5.1; Br, 46.1.

In some but not all experiments, the last (usually third) crop (mp 158–160 °C; 1.7–2.5 g, 10–15%) gave, on crystallization from acetone–light petroleum ether (1:1, ca. 15 mL each per g; recovery 60%), ivory prisms of the 4,6,8-tribromo isomer **14**, identical with authentic material (see below).

The final filtrates gave intractable sticky orange-brown resins. More **2** (corresponding to an additional 20–25% yield) was recoverable therefrom as the 1-acetoxy derivative **3** by subjecting the total resin to acetylation. Under the conditions specified below, the greater part of the acetylated product separated directly from the reaction mixture.

(b) Treatment of **5**[6] with 1 mol of bromine by the foregoing procedure gave **2** (yield 56%) identical with material obtained in a.

1-Acetoxy-4,4,8-tribromodiisophor-2(7)-en-3-one (3). A solution of **2** (2.56 g, 5 mmol) in glacial CH_3COOH (25 mL)–Ac_2O (12 mL) was treated dropwise at room temperature with 60% $HClO_4$ (8 drops); crystals separated after a few minutes. After 3 h of storage, the suspension was stirred into warm H_2O (250 mL) and the solid collected and washed neutral (mp 204–207 °C, 2.63 g, 95%, pure by IR). Crystallization from EtOH (50 mL per g, recovery 80%) or acetone–EtOH (12 and 20 mL per g, recovery 70%) gave prisms of **3**, mp 211–213 °C. Anal. Calcd for $C_{20}H_{27}Br_3O_3$: C, 43.3; H, 4.9; Br, 43.2. Found: C, 43.0; H, 4.9; Br, 44.0.

Hydrazinolysis of 2. A solution of **2** (3.08 g, 6 mmol) in hydrazine hydrate (12 mL)–EtOH (10 mL) was boiled for 5 min (temporary vigorous frothing), then stirred into ice (100 g), and acidified with concentrated HCl. The orange precipitate was collected immediately, washed neutral, and added *to* boiling EtOH (20 mL). The liquid rapidly deposited yellow 4-hydrazonodiisophor-2(7)-en-1-ol-3-one (**12**) (total yield, ca. 40%), identical (mmp 158–160 °C) with authentic material.[9]

4,4,8-Tribromo-1-ethoxydiisophor-2(7)-en-3-one (4). A stirred solution of 1-ethoxydiisophor-2(7)-en-3-one[14] (3.04 g, 10 mmol) in glacial CH_3COOH (50 mL) was treated dropwise with 1 M bromine in the same solvent (30 mL, 30 mmol); uptake of the third mole of halogen was slow. After 1.5 h, the pale-yellow liquid was stirred into ice–water (1.2 L) and the white precipitate crystallized from light petroleum ether (bp 40–60 °C, 50 mL), giving pale-yellow prisms of **4**, mp 130–132 °C (yield, 3.03 g, 56%). Anal. Calcd for $C_{20}H_{29}Br_3O_2$: C, 44.4; H, 5.4; Br, 44.3. Found: C, 44.4; H, 5.5; Br, 43.6.

4,4,8-Tribromo-1-carboxydiisophor-2(7)-en-3-one (8). (a) By Koch–Haaf Carboxylation of 2. To stirred concentrated H_2SO_4 (220 mL), kept below 0 °C by external cooling, was added 100% HCOOH (4 mL) dropwise over 5 min. Into the effervescing liquid, finely powdered **2** (10.25 g, 20 mmol) was introduced, each portion being allowed to dissolve before addition of the next (total, ca. 20 min). More HCOOH (20 mL) was dropped in during 45 min, and stirring was continued for another 1 h, the temperature being maintained near 0 °C throughout. Addition of the clear yellow liquid to ice–water gave a white precipitate (mp 225–228 °C, 10–10.5 g), which afforded on crystallization from acetone, lustrous platelets (8.4–9.3 g, 78–86%, in three successive crops) of **8**, mp 242–244 °C. UV: λ_{max} 213 nm (log ϵ 3.73), 274 (3.85). IR: 2960–2860 s, 1475 s, 1420 ms (CH_3, CH_2), 2640 m, 2540 mw (COOH), 1710 vs (CO of COOH), 1690 vs (CO ring), 1635 s (C=C conjug), 1395 ms, 1375 s (CMe_2), 1285, 1270 s d, 1225 ms, 1125 m, 1100 m, 1080 m, 945 m, 905 m, 805 mw, 755 mw, 725 ms, 705 mw, 675, 665 mw d cm^{-1}. MS, *m/e*: $M^{+\cdot}$ absent, 499, 497, 495, 493 vw (M – 45, COOH), 463, 461, 459 s (M – Br), 446, 444, 442 s (M – Br – 17, OH), 382, 380 w (M – 2Br), 375, 373, 371 w (M – Br – 71, C_5H_{11} – 17), 337, 335 ms (M – 2Br – 45), 301 vs (M – 3Br), 281, 279 s (M – 2Br – 56, C_4H_8 – 45), 266, 264 ms (M – 2Br – 71 – 45), 256 s (M – 3Br – 45), 230 s (M – 3Br – 71), 200 vs *max* (M – 3Br – 56 – 45), 185 vs (M – 3Br – 71 – 45), 201 s. Anal. Calcd for $C_{19}H_{25}Br_3O_3$: C, 42.2; H, 4.6; Br, 44.3. Found: C, 42.2; H, 4.7; Br, 44.6.

(b) Attempted Tribromination of 6. A stirred solution of **6**[2,14] (6.1 g, 20 mmol) in glacial CH_3COOH (100 mL) containing 60% HBr (0.3 mL) was treated dropwise during 1.5 h with 1 M bromine in glacial CH_3COOH (60 mL, 60 mmol); uptake of the third mole of halogen was slow. The resulting orange suspension was stirred into ice–water; the ivory precipiate was 4,8-*di*bromo-1-carboxydiisophor-2(7)-en-3-one, forming microprisms (from EtOH–hot H_2O, yield, 7.6 g, 82%), identical (mmp 218–220 °C) with authentic[6] material. Anal. Calcd for $C_{19}H_{26}Br_2O_3$: C, 49.4; H, 5.6; Br, 34.6. Found: C, 48.7; H, 5.6; Br, 35.6.

4,4,8-Tribromo-1-(methoxycarbonyl)diisophor-2(7)-en-3-one (9). A suspension of **8** (5.41 g, 10 mmol) in ether (200 mL) was treated with ethereal diazomethane (prepared[27] from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, Diazald, 6.4 g, 30 mmol). The reactant dissolved with effervescence; the yellow color of the reagent, initially discharged, finally persisted. After 2 h of storage at room temperature, the excess diazomethane was destroyed by the addition of CH_3COOH. Evaporation of the washed neutral ethereal phase gave a solid residue, which afforded pale-yellow prisms of **9**, mp 162–164 °C (from acetone–light petroleum ether; yield, 4.72 g, 85%). Anal. Calcd for $C_{20}H_{27}Br_3O_3$: C, 43.3; H, 4.9; Br, 43.2. Found: C, 42.95; H, 4.9; Br, 43.7.

1-(Methoxycarbonyl)diisophor-2(7)-en-3-one (7). Tribromination. (a) In Glacial Acetic Acid. A stirred solution of **7**[14] (6.35 g, 20 mmol) in glacial CH_3COOH (85 mL) was tribrominated by the standard procedure (see above). The resulting crude pale-yellow solid was washed neutral, air-dried (mp 114–122 °C, 10.5 g), and dissolved in acetone (40 mL)–light petroleum ether (10 mL), yielding successive crops of crystals. The initial massive prisms were **9**, mp and mmp (see above) 162–164 °C (2.0 g, 18%). The later microcrystalline material was the 4,8-dibromo analogue (5.35 g, 56%), identical (mmp 142–144 °C) with authentic material.[6] In identical experiments, the 4,8-dibromo compound was occasionally the only product (64–70%).

(b) In Diethyl Ether. A stirred solution of **7** (3.18 g, 10 mmol) in ether (30 mL) was treated dropwise during 15 min with bromine (6.0 g, 37.5 mmol) and stirred for a further 30 min. Addition of H_2O (50 mL), washing, drying (Na_2SO_4), and evaporation of the separated ethereal phase gave an orange oil, which was dissolved in EtOH–light petroleum ether (15 mL each). The resulting solid (3.5 g) gave, on crystallization from the same solvents, a first crop of **9**, mp 162–163 °C (1.55–1.75 g, 28–32%), and successive crops of the 4,8-dibromo analogue,[6] mp 142–144 °C (0.95–1.15 g, 20–24%).

4,4,8-Tribromo-1-carboxydiisophor-2(7)-en-3-one (8). (a) Action of Alkali. A solution of **8** (2.70 g, 5 mmol) in 1 M NaOH (50 mL, 50 mmol) was boiled under reflux for 2 h. The (cooled) pale-yellow liquid was slowly acidified with concentrated HCl (6 mL) and gave a precipitate (mp 193–196 °C, 1.35 g, 85%; pure by IR), affording white felted needles of 1,3-dicarboxyneodiisophora-2,7-diene (**10**), mp 213–215 °C (from acetone), identical with authentic material.[7]

(b) Methanolysis. A solution of **8** (5.40 g, 10 mmol) in MeOH (60 mL), treated with one of Na (1.15 g, 50 mmol) in the same solvent (50 mL) was boiled under reflux for 3 h, distilled to half volume, and added to ice–water containing concentrated HCl (5 mL). The resulting precipitate gave felted needles (1.35–1.65 g, 33–40%) of **4-bromo-1-carboxy-8-methoxy-6-methyl-5-nordiisophora-2(7),3,5-trien-3-ol** (**11**), mp 176–178 °C (from light petroleum ether). Anal. Calcd for $C_{20}H_{27}BrO_4$: C, 58.4; H, 6.6; Br, 19.45. Found: C, 58.5; H, 6.7; Br, 15.15.

4,4,8-Tribromo-1-(methoxycarbonyl)diisophor-2(7)-en-3-one (9). Methanolysis. A solution of **9** (1.40 g, 2.5 mmol) in MeOH (15 mL), treated with a solution of Na (0.29 g, 12 mmol) in the same solvent (15 mL) was refluxed for 6 h. The usual workup gave a product, forming after two crystallizations from acetone–light petroleum ether, microcrystalline **4-bromo-8-methoxy-1-(methoxycarbonyl)-6-methyl-5-nordiisophora-2(7),3,5-trien-3-ol,** mp 168–170 °C (yield, 45%). Anal. Calcd for $C_{21}H_{29}BrO_4$: C, 59.3; H, 6.8; Br, 18.8. Found: C, 59.9; H, 7.3; Br, 18.8.

4,6,8-Tribromo Compounds. 4,6,8-Tribromodiisophor-2(7)-en-1-ol-3-one (14). (a) A solution of 4-bromodiisophor-2(7)-en-1-ol-3-one[2] (**13**) (3.55 g, 10 mmol) in CCl_4 (60 mL) was treated with *N*-bromosuccinimide (3.56 g, 20 mmol) and benzoyl peroxide (0.3 g) and boiled under reflux for 45 min. Reaction occurred rapidly, succinimide rising to the surface of the liquid and forming a deposit on the walls. The mixture was kept at 0 °C for 2 h and filtered, the filtrate evaporated under reduced pressure, and the residual oil dissolved in light petroleum ether. The deposited solid gave, on crystallization from EtOH (ca. 25 mL per g), prisms (1.8–2.0 g, 35–40%) of **14**, mp 162–164 °C. Furth et al.[4] give mp 173–175 °C. Reducing the reaction time to 20 min did not improve yields. IR: 3510 vs (OH), 2980–2890 vs, 2870 s, 1475–1450 s mult (CH_3, CH_2), 1665 vs (CO), 1620 s (C=C conjug), 1400 s, 1385, 1375 vs d (CMe_2), 1320 vs, 1305 s, 1275 s, 1230 s, 1170 s, 1145 s, 1125, 1105, 1075 ms, 1045 vs, 905 ms, 870 mw, 840 m, 790 mw, 740 s, 710 s, 685 s, 665 mw, 640 mw cm^{-1}. MS, *m/e*: 516, 514, 512, 510 vvw ($M^{+\cdot}$), 499, 497, 495, 493 mw (M – 17), 445, 443, 441, 439 vs *max* (M – 71, C_5H_{11}), 435, 433, 431 m (M – Br), 364, 362, 360 mw (M – Br – 71), 283, 281 s (M – 2Br – 71), 202 vs (M – 3Br – 71), 201 s (M – 3Br – 71 – 1), 393, 391, 389 m, 365, 363, 361 m, 253 mw, 231 mw, 215 mw, 188 ms, 187 ms. Compare also ref 25.

(b) The use of **5**[6] (4.34 g, 10 mmol) and *N*-bromosuccinimide (10 mmol) in the foregoing procedure gave **14** in 20–25% yield.

The orange-brown resin remaining (in a or b) on spontaneous evaporation of the crystallization filtrates was subjected to perchloric acid catalyzed acetylation (conditions, see below) and gave the 1-acetoxy-*4,4,8*-tribromo compound **3** (12%), identical with authentic material described above. The mother liquors therefrom finally deposited the 1-acetoxy-*4,6,8*-tribromo compound **15** (8%), identical with authentic material described below.

(c) To a stirred solution of **1** (11.04 g, 40 mmol) in diethyl ether (100 mL), was added bromine (24 g, 7.7 mL, 150 mmol) dropwise during 20–30 min. Its color was discharged quickly at first, but more slowly later; on further stirring (1 – 1.5 h) crystalline solid appeared. To the pale-orange suspension was added H_2O (400 mL); the colorless crystalline solid (at the ether–water interface) was filtered off and rinsed successively with a little ether and light petroleum ether (solid S). The aqueous phase was extracted with more ether, and the combined ethereal orange solutions were washed neutral ($NaHCO_3$, H_2O) and dried (Na_2SO_4). The pale-

(27) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley: New York, 1967, Vol. 1, p 191; 1969, Vol. 2, p 102.

yellow resin remaining after the removal of the solvent was dissolved in light petroleum ether (60 mL, in portions) and gave successive crops (total, 9.2–10.3 g, 45–50%) of pale-yellow **14** (from light petroleum ether) identical with material obtained in a and b. Solid S was 14 (contributing up to 22% to the quoted yield). Spontaneous evaporation of the final mother liquors gave an intractable viscid dark-red resin.

In identical experiments, after isolation of the spontaneously separated, first crop of **14** (15–20%), the subsequent crops were the 4,4,8-tribromo isomer **2** (15–25%), and the final ones mixtures of both. The use of larger volumes of ether (300 + 2 × 50 mL) and slower rates of addition of bromine (80 min) gave **2** (45%) exclusively.

1-Acetoxy-4,6,8-tribromodiisophor-2(7)-en-3-one (15). A solution of 14 (1.54 g, 3 mmol) in glacial CH_3COOH (15 mL)–Ac_2O (8 mL) at ca. 40 °C was treated with external cooling with 60% $HClO_4$ (6 drops) which cleared the remaining turbidity. After 3 h of storage at room temperature, the solution was stirred into warm water (200 mL). The initially soft, later granular precipitate (84%) gave pale-yellow prisms of **15**, mp 153–155 °C (from EtOH–light petroleum ether, 1:1). Anal. Calcd for $C_{20}H_{27}Br_3O_3$: C, 43.3; H, 4.9; Br, 43.2. Found: C, 42.8; H, 4.9; Br, 42.8. The compound is considerably more soluble than its isomer **3**.

4,6,8-Tribromo-1-(methoxycarbonyl)diisophor-2(7)-en-3-one (17). A solution of 4,8-dibromo-1-(methoxycarbonyl)diisophor-2(7)-en-3-one (**5a**,[6] 2.38 g, 5 mmol) in warm CCl_4 (30 mL) was treated with *N*-bromosuccinimide (1.0 g, 5.5 mmol) and refluxed for 4 h under UV light (λ 254 nm). The usual workup (see above) gave a residual solid affording **17** as pale-yellow prisms, mp 181–183 °C (from acetone–light petroleum ether; yield, 75%). Anal. Calcd for $C_{20}H_{27}Br_3O_3$: C, 43.3; H, 4.9; Br, 43.2. Found: C, 43.7; H, 5.1; Br, 44.1.

4,6,8-Tribromodiisophor-2(7)-en-1-ol-3-one. Attempted Koch–Haaf reaction. The reactant (**14**) (5.1 g, 10 mmol) was subjected to the Koch–Haaf procedure[15] as described for its 4,4,8-tribromo isomer **2**; frothing was more extensive. The precipitate obtained when the liquid was stirred into ice–water gave, after being washed to neutrality, air-dried (4.8 g), and crystallized from acetone, pale-yellow prisms (1.4–2.1 g, 24–36%) of **1,4,6,8-tetrabromodiisophor-2(7)-en-3-one (18)**, mp 192–193 °C. Anal. Calcd for $C_{18}H_{24}Br_4O$: C, 37.5; H, 4.2; Br, 55.5. Found: C, 37.5; H, 4.2; Br, 54.7. Subsequent crops were mixtures of variable lower melting points consisting, according to their carbon NMR spectra, partially or wholly of 1-carboxylic acids retaining two or three bromine substituents, as well as the corresponding β-ketols, but their separation was not successful.

4-Bromo-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3,8-triol (19). A boiling solution of **14** (2.57 g, 5 mmol) in 1,4-dioxan (40 mL) was treated dropwise with 1 M NaOH (25 mL, 25 mmol) during 5–8 min (temporary turbidity) and boiled under reflux for 4 h. The liquid was distilled to half-volume and stirred into ice–water containing HCl (30 mmol). The precipitate gave, on crystallization from acetone–light petroleum ether (10 mL each), prisms (1.41 g, 76%) of **19**, mp 219–221 °C. Furth et al.[4] give mp 210 °C. UV: λ_{max} 222 nm (log ε 4.09), 297 (3.51). IR: 3365 vs br (OH), 2970–2890 vs, 1460 s, 1430 vs (CH_3, CH_2) 1395 s, 1375, 1365 s d (CMe_2), 850 mw, 820 m, 700 mw (? Ar), 1335 vs, 1305 s, 1230 s, 1165 ms, 1075 s, 1050 s, 1015 s, 995 vs, 965 s, 920 ms cm^{-1}. MS, *m/e*: 370, 368 ms ($M^{+\cdot}$), 352, 350 s (M − 18, H_2O), 319, 317 ms (M − 51, 3 × OH), 299, 297 vs (M − 71, C_5H_{11}), 281, 279 vs max (M − 71 − 18), 253 s (M − Br − 18 − 17 − 1), 238 s (M − Br − 3 × 17), 215 s (M − Br − 56, C_4H_8 − 18), 200 vs (M − Br − 71 − 18), 198 m (M − Br − 56 − 18 − 17), 334, 332 m, 296 vs, 295 vs, 294 vs, 293 s, 267 ms, 214 s. Anal. Calcd for $C_{18}H_{25}BrO_3$: C, 58.55; H, 6.8. Found: C, 58.0; H, 6.9.

4-Bromo-8-methoxy-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diol (20). A solution of **14** (2.57 g, 5 mmol) in methanol (25 mL) was treated with Na (0.58 g, 2.5 mmol) in MeOH (25 mL) and boiled under reflux for 6 h. Evaporation to half volume and addition to ice–water (150 mL) containing HCl (30 mmol) gave a precipitate, affording prisms (1.30 g, 68%) of **20**, mp 213–216 °C (from acetone–light petroleum ether). Anal. Calcd for $C_{19}H_{27}BrO_3$: C, 59.5; H, 7.05. Found: C, 60.1; H, 7.2.

4-Bromo-8-ethoxy-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diol (21). The identical procedure employing EtOH–EtONa gave the 8-ethoxy homologue **21**, forming microprisms (1.45 g, 72%), mp 158–160 °C (from light petroleum ether, bp 60–80 °C and 40–60 °C, 1:1). Furth et al.[4] give mp 156–158 °C. Anal. Calcd for $C_{20}H_{29}BrO_3$: C, 60.5; H, 7.3; Br, 20.1. Found: C, 60.3; H, 7.3; Br, 20.2.

8-Acetoxy-4-bromo-6-methyl-5-nordiisophora-2(7),3,5-triene-1,3-diol (22). A solution of **14** (2.57 g, 5 mmol) in hot glacial CH_3COOH (40 mL) treated with anhydrous potassium acetate (4.4 g, 45 mmol) was boiled under reflux for 1 h (severe "bumping" after a few minutes due to separated white solid). Addition of the suspension to ice–water (150 mL) gave a precipitate, affording prisms (1.0–1.15 g, 50–56%) of **22**, mp 199–201 °C (from acetone–light petroleum ether). Anal. Calcd for $C_{20}H_{27}BrO_4$: C, 58.4; H, 6.6. Found: C, 58.6; H, 6.6.

Attempted Hydrazinolysis of 14. Treatment of **14** with hydrazine under the conditions specified for the 4,4,8-tribromo isomer **2** (see above) gave crude products that resinified rapidly when attempts were made to crystallize them in the usual manner (e.g. from EtOH).

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Registry No. **1**, 6244-16-2; **1** (Et ether), 17204-30-7; **2**, 111557-61-0; **3**, 111557-62-1; **4**, 111557-63-2; **5**, 77871-11-5; **5a**, 111557-64-3; **5a** (acid), 111557-65-4; **6**, 68269-91-0; **7**, 68269-96-5; **8**, 111557-66-5; **9**, 111557-67-6; **10**, 111557-68-7; **11**, 111557-69-8; **11** (Me ester), 111557-70-1; **12**, 76557-53-4; **13**, 86949-89-5; **14**, 111557-71-2; **15**, 111557-72-3; **16**, 111557-73-4; **17**, 111557-74-5; **18**, 111557-75-6; **19**, 17336-85-5; **20**, 111557-76-7; **21**, 17471-18-0; **22**, 111557-77-8.

Supplementary Material Available: Comments elucidating the assignments of the carbon NMR spectra of Table II, spectral data (IR, MS) not appearing in the text for compounds **3**, **4**, **9**, **11**, **15**, **17**, **18**, **20**, **21**, and **22** (6 pages). Ordering information is given on any current masthead page.