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NOVEL BEHAVIOR OF 3,7- AND 5,7-DIBROMO-4-ISOPROPYLTROPOLONE ON BROMINATION; FORMATION OF THE ADDITION PRODUCT AND THE DIKETONE-TYPE TAUTOMER OF MONOCYCLIC TROPOLONES

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Many reports have been published on halogenation of 4-isopropyltropolone (hinokitiol) and it is known that this tropolone gave the monohalo- and dihalo substitution products bearing the halogen substituents at the 3-, 5- and/or 7-positions of the tropolone nucleus (1). 3,5,7-Tribromo-4-isopropyltropolone (I) have also been obtained on further bromination of the dibromo derivatives, 3,7-(II) and 5,7-dibromo-4-isopropyltropolone (III) (1a). Such a tropolone crowded with bulky substituents is of very interest not only in its physico-chemical properties but also in the mechanism of its formation. Present authors carried out further investigation on bromination of II and III, and now found that these tropolones firstly gave an addition product (IV) and a diketone-type tautomer (VII), respectively, as intermediates in the formation of the tribromo substitution product (I).

When a suspension of II in aqueous acetic acid (AcOH: H_2O=2:1) was treated with bromine at 0-5°C, two molar equivalents of the reagent was consumed rapidly and a pentabromo compound (IV), mp 115°C, $C_{10}H_9O_2Br_5$, was formed in a good yield. The original compound (II) was regenerated on heating of IV in ethanol. From this finding as well as the spectral evidence shown in Table 1, IV is concluded to have the structure, 3,5,6,7,7-pentabromo-4-isopropylcyclohept-3-ene-1,2-dione. When heated in tert.-butanol and then treated with p-toluidine, IV afforded a p-toluidine salt, mp 121-2°C (2), from which was obtained 3,5,7-tribromo-4-isopropyltropolone (I), mp 88-90°C (3) on the treatment with 6N sulfuric acid.

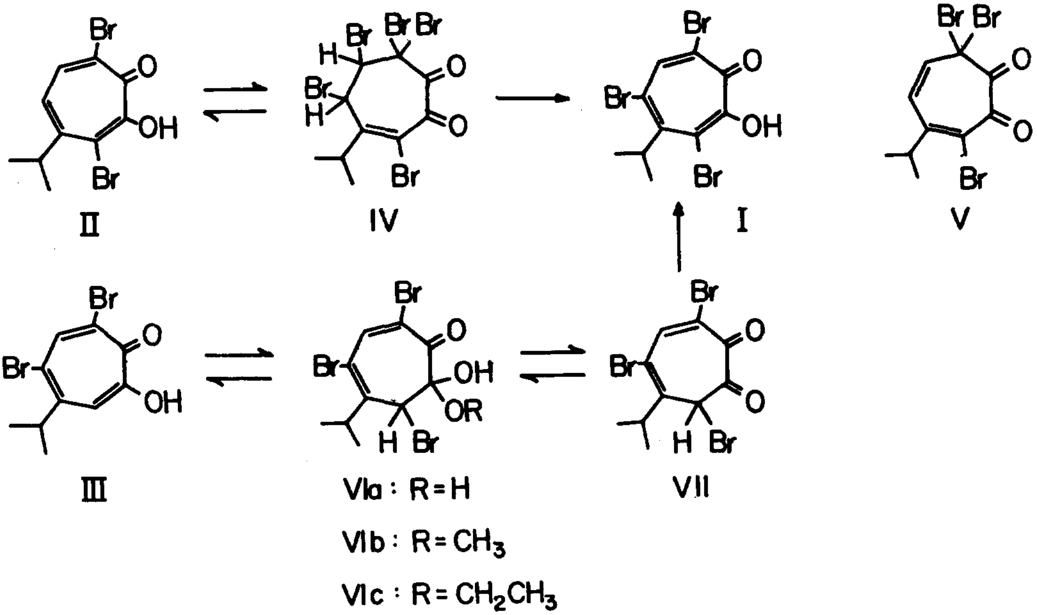
From the facts presented above, it becomes clear that the formation of I from II on the bromination in aqueous acetic acid is not attributable to the direct cationoid substitution at the 5-position, but to the addition-elimination reaction through the pentabromo compound (IV). The compound (IV) is thought to be formed on addition of bromine to the double bond of the tribromo compound (V) which should be produced primarily on the reaction of II with bromine. This consideration is supported from the fact that a tribromo compound, mp 79-80°C, $C_{10}H_9O_2Br_3$ corresponding to V; ir (KBr): 1785, 1724 cm^{-1} (α-diketone), was isolated from the reaction mixture although in only one of the experiments on bromination of II.

On the other hand, bromination of III in an aqueous acetic acid at 0-5°C resulted in a rapid consumption of a molar equivalent of bromine, giving a tribromo compound (VIa), mp 98-100°C, $C_{10}H_{11}O_3Br_3$; ir (KBr): 3390 (OH), 1681 (C=O), in a good yield. This compound (VIa) gave the original compound (III) on being heated in ethanol, whereas it resulted in dehydration on being heated in benzene or chloroform, giving another tribromo compound (VII), mp 108°C, $C_{10}H_9O_2Br_3$, which easily reproduced VIa by reverse hydration on being dissolved in aqueous acetic acid. From these results and the chemical evidence described below as well as the spectral evidence shown in Table. 1, the structure of VII is assigned to 3,5,7-tribromo-6-isopropylcyclohepta-3,5-diene-1,2-dione, and the structure of VIa is also assigned to the hydrate of VII. Although the structure of VII is corresponding to a diketo-form of 3,5,7-tribromo-4-isopropyltropolone (I), its enolization was not so easy; this was accomplished when heated in tert.-butanol and then treated with p-toluidine, giving a p-toluidine salt of I in a good yield. When bromination of III was carried out in methanol or in ethanol, a methyl hemiketal (VIb), mp 136°C, $C_{11}H_{13}O_3Br_3$, and an ethyl hemiketal (VIc), mp 99-101°C, $C_{12}H_{15}O_3Br_3$, were obtained in a good yield, respectively. These compounds (VIb and VIc) were also formed from both VIa and VII when dissolved in methanol or ethanol, respectively, and both VIb and VIc also gave VIa on being dissolved in aqueous acetic acid.

The compound (VII) is the first example of the diketone-type tautomer isolated on monocyclic tropolone. The unexpected stability of VII is thought to be

Table 1. The Spectral Data of the Bromo Compounds

Compounds	ir (KBr) cm^{-1}	nmr ($CDCl_3$) δ ppm		
		Isopropyl (4)	Other protons	
IV	1742, 1678 (C=O)	3.61 (1H, m)	5.20 (1H, d, J=2.5 Hz)	-CHBrCHBr-
		1.31 (3H, d, J=7 Hz)	5.47 (1H, d, J=2.5 Hz)	
		1.34 (3H, d, J=7 Hz)		
VIb	3436 (OH)	3.11 (1H, m)	7.78 (1H, s)	$-\overset{|}{C}=CH-$
	1684 (C=O)	1.24 (3H, d, J=7 Hz)	5.16 (1H, s)	OH
		1.10 (3H, d, J=7 Hz)	4.74 (1H, s)	-CHBr-
			3.77 (3H, s)	OCH_3
VIc	3470 (OH)	3.38 (H, m)	7.80 (1H, s)	$-\overset{|}{C}=CH-$
	1672 (C=O)	1.25 (3H, d, J=7 Hz)	4.79 (1H, s)	-CHBr-
			2.98 (2H, m)	OCH_2CH_3
			1.23 (3H, t, J=7 Hz)	
VII	1701, 1689 (C=O)	3.50 (1H, m)	7.64 (1H, s)	$-\overset{|}{C}=CH-$
		1.28 (3H, d, J=7 Hz)	5.03 (1H, s)	-CHBr-
		1.12 (3H, d, J=7 Hz)		



due to the steric interaction between the vicinal substituents, the isopropyl group and bromines, which are prevented to arrange in the same plane on enolization. Some diketone-type tautomers of trihalo-4-isopropyltropolone, 5,7-dibromo-3-chloro, 3,7-dibromo-5-chloro-, 7-bromo-3',5-dichloro- and 3,5,7-trichloro-6-isopropylcyclohepta-3,5-diene-1,2-dione, similar to VII, were also obtained by the dehydration of hydrates which formed on bromination or chlorination of the corresponding 5,7-dihalo-4-isopropyltropolones. These diketones could also be enolized to 3,5,7-trihalo-4-isopropyltropolone as VII did. However, any attempts on the reverse change from I to VII was not achieved.

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2) The melting point of p-toluidine salt has been reported as 125-6°C (1a).

3) Two kinds of the tribromo derivatives, " α-tribromohinokitiol ", mp 96°C, and " β-tribromohinokitiol ", mp 90-91.5°C, have been reported (1a). The compound (I) is identical with the latter.

4) On these compounds two methyl groups of the isopropyl group are magnetically unequivalent.