CHEMISTRY LETTERS, pp. 1229-1232, 1974. Published by the Chemical Society of Japan

HALOGENATION OF 2,3-HOMOTROPONE. SYNTHESES OF HALO-SUBSTITUTED 2,3-HOMOTROPONES

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Bromination of 2,3-homotropone (1) with molecular bromine gave two dibromides, (3) and (4). Chlorination of (1) with sulfuryl chloride proceeded in a different manner to give four dichlorides, (8), (9), (10), and (11). These dihalides were easily converted into halo-substituted 2,3-homotropones, (6), (7), (12), and (13), on treatment with bases.

Only a few investigations have been reported on the chemical properties of 2,3-homotropone (1) since it was first prepared by Pettit et al.[1~3] We have recently reported a simple way to prepare (1) from cyclooctadienes or 1,3,5-cyclooctatriene via 6-bromo-2,4-cyclooctadienone (2).[4] We wish here to report that halogenation-dehydrohalogenations of (1) readily lead to halo-substituted 2,3-homotropones.

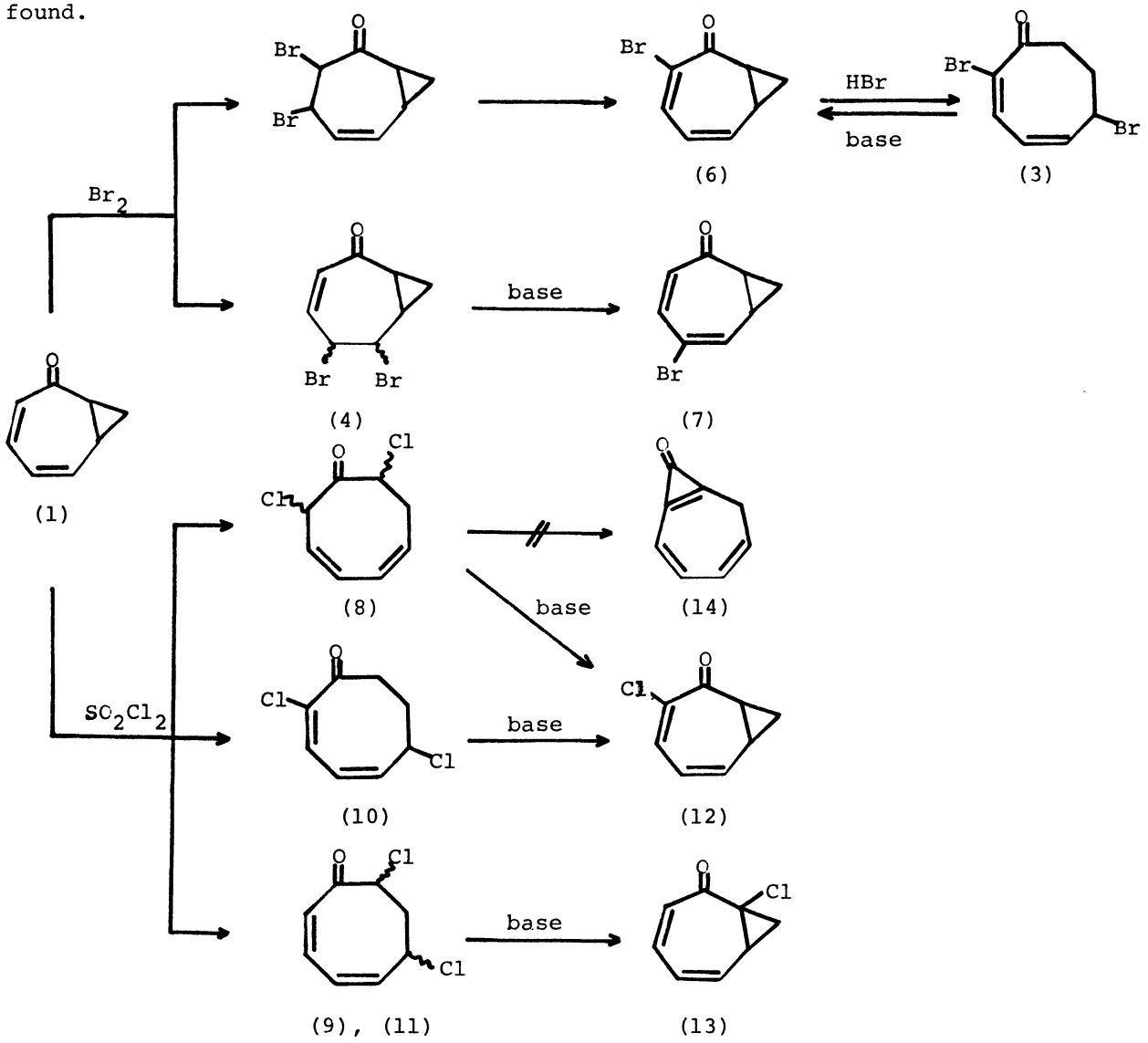
Reaction of (1) with molecular bromine in methylene chloride at -65°C gave 2,6-dibromo-2,4-cyclooctadienone (3) and 5,6-dibromobicyclo[5.1.0]oct-3-en-2-one (4) (colorless needles, mp 92°C , in the order of decreasing Rf value on silica-gel tlc, in 30.2% and 55.0% yield, respectively. (3) may be formed by addition of bromine to 6,7-double bond of (1) followed by dehydrobromination giving (6) and subsequent addition of the liberated hydrogen bromide to the cyclopropane ring. In fact, (6), on treatment with anhydrous hydrogen bromide in methylene chloride, underwent ring opening of the cyclopropane ring to give (3), probably via a 2-hydroxyhomotropylium bromide. Although (4) is formed stereospecifically, the stereochemistry is not yet certain.

Treatment of (3) and (4) with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in methylene chloride at room temperature or with triethylamine at higher temperature gave 7-bromo-2,3-homotropone (6) and 5-bromo-2,3-homotropone (7), respectively, in

quantitative yields.

On chlorination with sulfuryl chloride in methylene chloride at -50°C, (1) behaved in a different manner and gave 2,8-dichloro-3,5-cyclooctadienone (8), 6,8-dichloro-2,4-cyclooctadienone (9), 2,6-dichloro-2,4-cyclooctadienone (10), and the stereoisomer of (9), (11), in 30.8%, 44.4%, 5.1%, and 11.7% yield, respectively. The compound (8) may be formed by addition of chlorine in a manner of 1,6-addition with cleavage of the 2,3-bond in the cyclopropane ring, and (9) and (11) by 1,2-addition to the cyclopropane ring.

On treatment with DBN, (8) and (10) gave 7-chloro-2,3-homotropone (12), while (9) and (11) gave 2-chloro-2,3-homotropone (13) in quantitative yields. Although (8) was expected to produce the cycloheptatrienocyclopropenone (14) with base as 2,8-dibromocyclooctanone does cycloheptenocyclopropenone,[5] no trace of (14) was found.



Table

Spectral Data of The Dihalides and Halo-substituted 2,3-Homotropones

Compound	ir cm^{-1}[a]	uv nm[b] (log ε)	^{1}H-nmr ppm[c] (J Hz)	(assignment)
	1680	292 (3.86)	7.35 d (5.9)	1H (H-3)
(3)	1626		6.49 dd (11.5, 7.6)	1H (H-5)
	1575		6.11 dd (11.5, 5.9)	1H (H-4)
			4.63 m	1H (H-6)
			3.2-2.2 m	4H
	1648[d]	217 (4.07)	6.23 ddd (13.0, 5.0, 1.8)	1H (H-4)
(4)	1625		5.92 d (13.0)	1H (H-3)
			5.23 m	2H (H-5,6)
			2.5-1.5 m	4H
	1740	231 (3.71)	6.2-5.8 m	4H
(8)	1624	300 (3.10)	5.47 d (5.0)	1H (H-2)
			4.77 dd (7.0, 4.1)	1H (H-8)
			2.8 m	2H (H-7,7')
	1652	283 (3.76)	6.7-6.1	3H (H-3 5)
(9)	1600		5.94 dd (13.0, 1.2)	1H (H-2)
			4.85 br. dd (12.0, 6.5)	1H (H-8)
			4.55 m	1H (H-6)
			3.2-2.4 m	2H (H-7,7')
	1677	287.5 (3.82)	7.01 dd (6.0, 2.1)	1H (H-3)
(10)	1628		6.6-6.1 m	2H (H-4,5)
	1576		4.55 m	1H (H-6)
			3.2-2.2 m	4H
	1676	272.5 (3.79)	6.8-6.3 m	3H (H-3,5)
(11)	1620		6.15 d (13.0)	1H (H-2)
	1595		4.81 dd (10.8, 7.5)	1H (H-8)
			4.6 m	1H (H-6)
			3.9-3.5 m	2H (H-7,7')
	1640	310 (3.67)	7.03 d	1H (H-6)
(6)	1562	360 sh(3.21)	6.65 dd (11.5, 7.1)	1H (H-4)
			5.63 dd (11.5, 0.6)	1H (H-5)
			2.66 ddd (9.5, 7.8, 6.6)	1H (H-2)
			2.4-1.4 m	3H
	1640	219.5 (4.05)	6.95 br. d (6.0)	1H (H-4)
(7)	1612	301 (3.43)	6.46 dd (13.0, 1.5)	1H (H-6)
	1580	345 sh(3.00)	5.78 ddd (13.0, 1.5, 0.9)	1H (H-7)
			2.48 dddd(9.0, 9.0, 6.0, 1.5)	1H (H-2)
			2.2-1.5 m	3H
	1650	224 (3.69)	6.71 d (8.2)	1H (H-6)
(12)	1572	306.5 (3.59)	6.57 ddd (11.5, 8.2, 0.7)	1H (H-5)
		355 sh(3.11)	5.67 dd (11.5, 6.6)	1H (H-4)
			2.62 ddd (9.5, 7.7, 6.5)	1H (H-2)
			2.4-1.3 m	3H
	1660	286 (3.59)	6.49 ddt (11.0, 7.5, 0.9)	1H (H-4)[e]
(13)	1640	332 sh(3.10)	6.42 ddd (12.5, 6.8, 0.9)	1H (H-6)
	1592		6.01 dt (12.5, 0.9)	1H (H-7)
			5.83 ddt (11.0, 6.8, 0.9)	1H (H-5)
			2.63 dddd(10.0, 8.6, 7.5, 0.9)	1H (H-3)
			2.27 dd (10.0, 5.5)	1H (H-8 exo)
			2.08 dd (8.6, 5.5)	1H (H-8 endo)

a) in liquid film unless noted. b) in ethanol. c) in CCl_4 at 60 MHz unless noted. d) in KBr disk. e) in CCl_4 at 100 MHz.

When the crude mixture of dibromides was treated with DBN, a ca 1:1 hardly separable mixture of (6) and (7) was obtained in high yield. The mixture of dichlorides, on the other hand, gave by a similar treatment a mixture of (12) and (13) (38:62 by vpc) which was able to be separated by silica-gel column chromotography.

The structures of dihalides and halo-substituted 2,3-homotropones were determined by means of elemental analyses and spectroscopy which are summarized in the Table. The 100 MHz ^{1}H-nmr and nmdr spectra of (13) revealed the detailed coupling constants which are in good agreement with those reported for 8-exo-ethoxycarbonyl-2,3-homotropone by Soma et al.[6] While the ^{1}H-nmr spectra of these halo-2,3-homotropones, as already pointed out in the literatures for the parent compound[1,7], do not show existence of appreciable delocalization, the uv and ir spectra seem to indicate some delocalization. Easy regeneration of 2,3-homotropone-skeleton from the dihalides may indicate that a 2,3-homotropone is stabilized to some extent by delocalization.

It may be expected that 2-chloro-2,3-homotropone (13) produces 2,3-cyclopropenotropone by dehydrochlorination. Such attempts are now in progress.

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(Received August 20, 1974)