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Reactions of 2,4,4,6-Tetrabromo-2,5-cyclohexadien-1-one with Alkenes in the Presence of Weak Bases[1]

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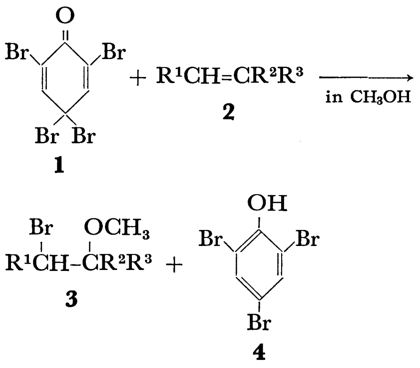
Schmidt and his co-workers[2] reported on the formation of 1-bromo-2-methoxycyclohexane by the reaction of 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one (**1**) with cyclohexene in methanol. As with other 4-bromo-2,5-cyclohexadien-1-ones,[3] one of the bromine atoms at the 4-position in **1** is presumed to react as a bromonium species in the reaction. This paper deals with the reaction of **1** with alkenes in the presence of several weak bases.

β-Bromo-*α*-methoxyethylbenzene (**3a**) was obtained in good yield by the reaction of **1** with styrene in methanol. Under similar conditions, *β*-bromo-*α*-methoxyethyl *n*-butyl ether (**3b**) and 4-bromo-3-methoxy-3-methyl-1-butene (**3c**) were obtained from *n*-butyl vinyl ether and isoprene, respectively. The reaction conditions and the results are summarized in Table 1.

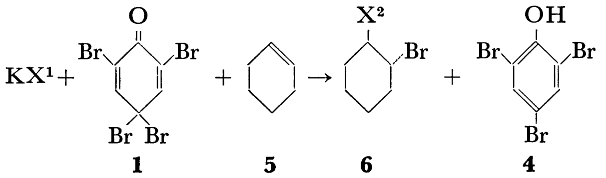


	2a,3a	2b,3b	2c,3c
R^1	C_6H_5	n-C_4H_9O	H
R^2	H	H	CH_3
R^3	H	H	$CH=CH_2$

It can be assumed that in the addition process a transitory bromonium species is formed in the initial step by the attack of a nucleophilic reagent under mild conditions, and then the bromonium species reacts with the double bond in alkenes.

The above addition reaction was further applied to the preparation of some bifunctional adducts of cyclohexene, which can be used for syntheses.

trans-1-Bromo-2-hydroxycyclohexane (**6a**),[4] *trans*-1-bromo-2-chlorocyclohexane (**6b**), *trans*-1,2-dibromocyclohexane (**6c**), and *trans*-1-acetoxy-2-bromocyclohexane (**6d**) were obtained by the reaction of **1** with cyclohexene in the presence of various bases (see Table 1).



	a	b	c	d
X^1	p-$CH_3C_6H_4SO_3$	Cl	Br	CH_3CO_2
X^2	OH	Cl	Br	CH_3CO_2

These reactions are suitable for the preparation of bifunctional adducts of alkenes in view of simple procedure, mild conditions, and high yield.

Experimental

All melting points and boiling points are uncorrected. The mass spectra were measured with a Hitachi RMU-6L spectrometer; ionizing voltage: 70 eV, evaporation temperature: 95°C. The NMR spectra were obtained with a Japan

TABLE 1. SUMMARY OF THE REACTIONS OF **1** WITH ALKENES

Alkene	(mmol)	**1** (mmol)	Nucleophile	(mmol)	Temp. (°C)	Time (hr)	3 or 6	Bp (°C/mmHg)	Yield[a] (%)	4 Yield[a] (%)
2a	2.6	1.3	$CH_3OH^{b)}$		−2— 4	1.5	**3a**	116—119/17	91	92
2b	3.0	1.5	$CH_3OH^{b)}$		4	1.5	**3b**	84— 86/15	88	100
2c	6.0	3.0	$CH_3OH^{b),f)}$		2	2.5	**3c**	71— 76/24	67	97
5	1.0	1.0	p-$CH_3C_6H_4SO_3K^{c)}$	1.0	4	2.5	**6a**	93/18	53	62
5	2.2	2.0	$KCl^{c),e)}$	3.0	5—21	4.0	**6b**	87— 89/18	29	95
5	2.2	2.0	$KBr^{c),f)}$	3.0	3— 7	2.5	**6c**	99—101/16	75	97
5	2.2	2.0	$CH_3CO_2K^{d)}$	3.0	26	72	**6d**	115—117/19	76	94

a) Based on **1**. b) Used as a reacting solvent. c) A dioxane-water mixture (3: 1) (40 m*l*) was used as a solvent. d) Acetic acid (30 m*l*) was used as a solvent. e) Concentrated hydrochloric acid (2 m*l*) was added. f) *p*-Toluenesulfonic acid monohydrate was added per mol of **1**.

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[1] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971: Preprints, III, p. 1585.

[2] E. Schmidt, A. Aschel, and W. von Knilling, *Ber.*, **59**, 1876 (1926).

[3] B. Miller, *J. Org. Chem.*, **28**, 345 (1963).

[4] The hydroxy group in **6a** (in this case) is presumably a result of the addition of solvent water.

Electron Optics, JNM-6C spectrometer, using TMS as an internal standard. The IR spectra were recorded in neat liquid using a JASCO model IR-G spectrophotometer (Japan spectroscopic Co., Ltd.). The GLC data were obtained with a GCG-550T apparatus (Yanagimoto Mfg. Co., Ltd.), using a column containing 5% silicone SE-30 on Celite 545 AW.

Materials. Compounds **3a**—**c** were characterized by NMR and mass spectra.

3a: NMR (in CCl_4): 6.68 (CH_3, s), 6.54 (CH_2, q), 5.63 (CH, t), 2.65 (C_6H_5, s): Mass: *m/e* 216, 214 ($C_6H_5CH(OCH_3)$-CH_2Br), 185, 183 ($C_6H_5CHCH_2Br$), 121 ($C_6H_5CHOCH_3$): (Found: Br, 36.7%).

3b: NMR (in CCl_4): 9.05 (CH_3, m), 8.52 (CH_2, m), 6.70 ($BrCH_2$, d), 6.65 (OCH_3, s), 6.45 (OCH_2, m), 5.41 (OCH, t): Mass: *m/e* 181, 179 ($BrCH_2CHOC_4H_9$-*n*), 139, 137 ($BrCH_2CHOCH_3$), 117 ($CH_3OCHOC_4H_9$-*n*): (Found: Br, 36.2%).

3c: NMR (in CCl_4): 8.65 (CH_3, s), 6.83 ($BrCH_2$, s), 6.72 (OCH_3, s), 4.85, 4.70, 4.43 ($CH{=}CH_2$): Mass: *m/e* 165, 163 ($CH_2{=}CHC(OCH_3)CH_2Br$), 99 ($CH_2{=}CHC(OCH_3)$-$(CH_3)CH_2$), 85 ($CH_2{=}CHC(OCH_3)CH_3$), 55 ($CH_2{=}CHCH$-CH_3).

The structures of **6a**—**d** were confirmed by direct comparison of their retention times in GLC and IR spectra with those of authentic samples.[5-7]

2,4,4,6-Tetrabromo-2,5-cyclohexadien-1-one (1). Bromine (8.0 g, 5 mmol) was added in small portions to a solution of 2,4,6-tribromophenol (12.3 g, 4 mmol) in methanol-acetic acid (1 : 1) (60 m*l*) at 2—3°C. After 1 hour, 10% aqueous sodium carbonate solution (50 m*l*) was added. The yellow precipitates were collected, washed with water and methanol, and dried over anhydrous phosphorus pentoxide in a vacuum desiccator. Yield, 15.0 g (90%), mp 136°C (dec.) (lit.[8] 125°C (dec.)).

Reaction of 1 with an Alkene. As a typical example, the reaction of 1 with styrene is described: (for details, see Table 1). To a well-stirred solution of styrene (**2a**) (2.6 mmol) in methanol, **1** (1.3 mmol) was added at −2—4°C. Stirring was continued for 1.5 hr (solid **1** disappeared), the reaction mixture was poured into 10% aqueous sodium carbonate solution, and the aqueous layer was extracted with *n*-hexane. The organic layer was washed with water and dried over anhydrous potassium carbonate. After *n*-hexane was evaporated, the residue was distilled under reduced pressure to afford **3a** (91%), bp 116—119°C/17 mmHg. The carbonate solution was acidified with concentrated hydrochloric acid, and the precipitates were filtered and washed with water to give 2,4,6-tribromophenol, mp 91—93°C (92%).

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5) S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2780 (1942).

6) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

7) H. R. Snyder and L. A. Brooks, "Organic Syntheses," Coll. Vol. II, p. 171 (1943).

8) R. Benedikt, *Ann. Chem.*, **199**, 127 (1879).