Positive Halogen Compounds. V. *t*-Butyl Hypobromite and Two New Techniques for Hydrocarbon Bromination[1]

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t-Butyl hypobromite has been prepared and characterized. It smoothly brominates hydrocarbons by a photoinduced free radical process analogous to chlorination by *t*-butyl hypochlorite, and competitive experiments indicate that the *t*-butoxy radical acts as a chain carrier. Halogenation with *t*-butyl hypochlorite in the presence of bromotrichloromethane also produces alkyl bromides in some systems, and the technique may be useful for the bromination of otherwise unreactive hydrocarbons.

The utility of *t*-butyl hypochlorite as a free radical halogenating agent, reacting by the chain propagating sequence[3]

$$(CH_3)_3C{-}O\cdot + RH \longrightarrow (CH_3)_3C{-}OH + R\cdot \tag{1}$$

$$R\cdot + (CH_3)_3C{-}OCl \longrightarrow RCl + (CH_3)_3C{-}O\cdot \tag{2}$$

suggested to us the possibility of a parallel bromination by *t*-butyl hypobromite, by a scheme in which (2) would be replaced by

$$R\cdot + (CH_3)_3C{-}OBr \longrightarrow RBr + (CH_3)_3C{-}O\cdot \tag{3}$$

The ultraviolet spectra of dilute solutions of *t*-butyl hypobromite have been examined by Anbar,[4] and a crude preparation has recently been described by Kergomard.[5] However, the material has not been isolated in the pure state, nor adequately characterized.

Attempts to prepare *t*-butyl hypobromite from halogen, alkali, and *t*-butyl alcohol (a method successful for the preparation of *t*-butyl hypochlorite)[6] yield no product, presumably because of unfavorable equilibria. However, reaction of *t*-butyl alcohol with aqueous hypobromous acid (free of Br^-) and extraction of the product with trichlorofluoromethane gives the hypobromite in 42% yield.

Prepared in this way, *t*-butyl hypobromite is a reddish orange liquid, which is stable for long periods in the cold and dark, can be vacuum distilled, but decomposes rapidly at about 85°. Further physical properties are given in the Experimental part of this paper. It is decomposed by repeated washing with water, immediately by 5% sodium bicarbonate solution.

Irradiation (incandescent light) in inert solvent or alone gives acetone and methyl bromide *via* the same sort of chain process as in the decomposition of the hypochlorite. Solutions in cyclohexene are also stable in the cold and dark. Addition of acetic acid leads to rapid reaction, presumably to give acetoxy bromide *via* polar addition. The radical bromination to give 3-bromocyclohexene occurs photochemically in a few minutes at room temperature. Similarily, toluene gives benzyl bromide, ethylbenzene gives α-bromoethylbenzene, cyclohexane gives cyclohexyl bromide, cyclobutane gives cyclobutyl bromide, and propylene gives allyl bromide.

In each case the reactions parallel very closely the corresponding chlorinations with *t*-butyl hypochlorite, and, as a demonstration that the same chain carrier (the *t*-butoxy radical) is involved in both halogenations, several competitive halogenations were carried out with *t*-butyl hypobromite and relative reactivities compared with those previously reported for *t*-butyl hypochlorite.[3] Results appear in Table I, and agreement is excellent. It should also be noted that the order of reactivities is quite different from that observed in bromine atom reactions,[7] showing that bromine atoms play no significant part in the chain propagation process. Since the same chain carrier is involved, we expect that *t*-butyl hypobromite should be as versatile a halogenating agent as the hypochlorite, giving the same isomer distribution of halides, and usable when bromides are desired.

TABLE I

RELATIVE REACTIVITIES OF HYDROCARBONS IN *t*-BUTYL HYPOHALITE HALOGENATIONS AT 40° (PER MOLECULE, TOLUENE TAKEN AS UNITY)

	Rel. react.	
Compound	ROBr	ROCl[a]
Cyclohexane	6.20 ± 0.25	6.00 ± 0.09
2,3-Dimethylbutane	2.96 ± .15	3.18 ± .12
Cumene	2.76 ± .15	2.80 ± .15
Ethylbenzene	2.45 ± .15	2.30 ± .12
Toluene	1.00	1.00

[a] See ref. 3.

The fast reaction of many hydrocarbon radicals with bromotrichloromethane also suggested an alternative way of preparing alkyl bromides through a *t*-butoxy radical chain *via* the sequence

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(2) Columbia University Fellow, 1961–1962.

(3) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(4) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

(5) A. Kergomard, *Bull. soc. chim.*, **12**, 2360 (1961).

(6) A. M. Teeter and E. W. Bell, *Org. Syn.*, **32**, 20 (1952).

(7) For discussion and data on bromine atom reactions, *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, Chap. 8.

$$BuO\cdot + RH \longrightarrow BuOH + R\cdot \tag{4}$$

$$R\cdot + CCl_3Br \longrightarrow RBr + CCl_3\cdot \tag{5}$$

$$CCl_3\cdot + BuOCl \longrightarrow BuO\cdot + CCl_4 \tag{6}$$

using the more easily available *t*-butyl hypochlorite. It should be noted that this is a different scheme than the direct bromination using bromotrichloromethane recently studied by Huyser,[8] since the point of attack on the hydrocarbon is determined by the *t*-butoxy radical rather than a $\cdot CCl_3$ radical which can also yield alkyl bromide. Further, the

$$CCl_3\cdot + RH \longrightarrow CHCl_3 + R\cdot \tag{7}$$

success of the scheme depends upon reaction 5 competing with reaction 2 which would bypass the bromotrichloromethane and yield alkyl chloride. Table II summarizes our experiments, and illustrates the limitations of the method: first, slow addition of *t*-butyl hypochlorite is required to maintain a high bromotrichloromethane/hypochlorite ratio and favor (5) over (2); second, the competition is successful only with a reactive, nonresonance-stabilized R· radical. This is a plausible result, since the attack of a benzyl radical on bromotrichloromethane is probably an endothermic process. The last experiment in Table II also serves to confirm the role of the *t*-butoxy radical as the chain carrier, since the ratio of total cyclohexyl halides to benzyl halides produced was approximately 6 (compare Table I).

TABLE II

REACTIONS OF *t*-BUTYL HYPOCHLORITE AND BROMOTRICHLOROMETHANE WITH HYDROCARBONS (MOLE RATIOS TO HYPOCHLORITE IN PARENTHESES)

Hydrocarbon	CCl_3Br	{—Product, %—} RCl	 RBr
Cyclohexane (3)	(1)	97	3
(3)	(3)	95	5
(3)	(2 + 3)[a]	6	94
Cyclobutane (3)	(2 + 3)[a]	3	97
Toluene (3)	(3)	100	0
(3)	(2 + 3)[a]	97	3
Cyclohexane (2)[b]	(2 + 3)[a]	8	75
Toluene (2)[b]		16	0

[a] *t*-Butyl hypochlorite in 3 moles of bromotrichloromethane added dropwise over 3–4 hr. with irradiation to system containing 2 moles of bromotrichloromethane. [b] Cyclohexane and toluene both present.

The predicted ratio for bromination by bromotrichloromethane alone, reactions 5 and 7, would be less than unity.[7] Although bromotrichloromethane–*t*-butyl hypochlorite bromination thus appears to be limited to hydrocarbons with strong C—H bonds which yield reactive radicals, it may still be of some utility, since these are precisely the molecules which are not easily brominated by usual reagents such as bromine or N-bromosuccinimide, and the method does not require the preparation of *t*-butyl hypobromite.

Experimental

***t*-Butyl Hypobromite.**—Silver sulfate was added in small portions to 0.2 mole of bromine in distilled water until the bromine color was discharged (0.24 mole required). The resulting solution of hypobromous acid was decanted from precipitated silver bromide and shaken for 15 min. with *t*-butyl alcohol (0.18 mole) dissolved in 150 ml. of trichlorofluoromethane (Freon 11). The nonaqueous layer was separated, washed once with water, dried over sodium sulfate, and distilled under reduced pressure to give 43% *t*-butyl hypobromite, b.p. 44–45°/85 mm.; purity by titration[3] 99.4%.

The *t*-butyl hypobromite prepared in this way was a reddish orange liquid with a penetrating bromine-like odor, m.p. −27 to −28°, n^{26}_D 1.4488, d^{25}_4 1.3347. The ultraviolet spectrum showed λ_{max} 280 mμ, ϵ_{max} 120 and a long tail absorption extending into the visible region. The infrared spectrum was almost identical with *t*-butyl hypochlorite, but with a band (presumably RO—Br) at 15.6 μ in carbon tetrachloride. The hypobromite is stable in the dark at 0° for long periods, but decomposes on heating to 85°, or on irradiation. Examination of the decomposition products on irradiation in carbon tetrachloride by gas-liquid chromatography (GLC) revealed major peaks corresponding to acetone and methyl bromide. It is also destroyed by repeated washing with water, or immediately by 5% sodium bicarbonate solution.

Brominations with *t*-Butyl Hypobromite.—Solutions of the hypobromite in cyclohexene are stable for weeks in the cold and dark, although addition of acetic acid leads to rapid loss of hypobromite color, presumably *via* a polar addition reaction. Irradiation of the solution also leads to rapid reaction, giving 3-bromocyclohexene, identified by GLC retention time and infrared spectra of samples purified by GLC. Similar photobrominations were carried out with other hydrocarbons in small sealed, degassed tubes, and products identified by GLC retention and infrared spectra as follows: cyclohexane, giving cyclohexyl bromide; toluene, giving benzyl bromide; ethylbenzene giving predominantly α-bromoethylbenzene; and propylene, giving allyl bromide. Reactions were in general, complete in 20 min. at room temperature, and no other significant products were detected.

Competitive reactions were carried out in sealed tubes with GLC analysis for unchanged hydrocarbon using an internal standard precisely as in previous work with *t*-butyl hypochlorite.

Halogenations with *t*-Butyl Hypochlorite in Bromotrichloromethane.—Reactions involving slow addition of hypochlorite were carried out in a small stirred flask with illumination under nitrogen with times and quantities of materials shown in Table II, and analyzed by GLC. Other experiments were in sealed tubes.

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(8) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).