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Reaction of N-Haloamide. XVII.[1] Bromo-formyloxylation of Olefins with N,N-Dibromobenzenesulfonamide and Formic Acid

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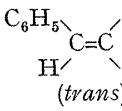
A convenient method for β-bromo-formyloxylation of olefins with N,N-dibromobenzenesulfonamide and formic acid was developed. Cyclohexene, styrene, *trans*-β-methylstyrene, and 1- hexene were made to react to give *trans*-2-bromocyclohexyl formate (I), 2-bromo-1-phenylethyl formate (II), *erythro*-2-bromo-1-phenylpropyl formate (III), and 1-bromo-2-hexyl fromate (IV).

We have recently reported[3] that the reaction of N,N-dibromobenzenesulfonamide (DBBS) with cyclohexene in formamide or dimethylformamide gave a product, *trans*-2-bromo-1-cyclohexyl N-benzenesulfonylformimidate or N,N-dimethyl-N′-benzenesulfonylformamidine, respectively, besides minor products, *trans*-2-bromo-1-cyclohexyl formate and other compounds.

It seemed noteworthy that the addition of formamides on the intermediary bromonium ion occurred with not their nitrogen atoms but oxygen ones. These results suggested a direct route to obtain β-bromo-formates though their yields were poor in above reactions, accordingly we have attempted to improve the reactions to give desired bromo-formates in good yields using formic acid and DBBS.

Various methods to obtain β-halo-formyloxy compounds from olefins have been reported,[4–8] among them, the method presented here by us may be characterized with regard to its convenient procedures and good yields.

Table I. Olefins and Products

Olefin	Product		bp °C (mm/Hg)	Yield (%)
		I	79— 86 (5)	68
C_6H_5–CH=CH_2	C_6H_5–CH(OCHO)–CH_2Br	II	111—113 (6)	65
 (*trans*)	C_6H_5–CH(OCHO)–CHBrCH_3	III	115—121 (7)	74
$CH_3(CH_2)_3CH$=CH_2	$CH_3(CH_2)_3$CH(OCHO)–CH_2Br	IV	66— 69 (5)	59

1) Part XVI: H. Terauchi, S. Takemura, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **20**, 2477 (1972).
2) Location: *Kowakae, Higashi-Osaka-Shi, Osaka-fu.*
3) S. Takemura, H. Niizato, and Y. Ueno, *Chem. Pharm. Bull.* (Tokyo), **19**, 1606 (1971).
4) F. Boerwinkle and A. Hassner, *Tetrahedron Letters*, **1968**, 3921.
5) D.R. Dalton, R.C. Smith, Jr., and D.G. Jones, *Tetrahedron*, **26**, 575 (1970).
6) E. Schmidt, R. Schumacher, and R. Asmus, *Ber.*, **56**, 1240 (1923).
7) K. Morita, S. Noguchi, H. Kono, and T. Miki, *Chem. Pharm. Bull.* (Tokyo), **11**, 90 (1963).
8) T.R. Carrington, S. Eardley, J. Elks, G.F.H. Green, G.I. Gregory, A.G. Long, and J.C.P. Sly, *J. Chem. Soc.*, **1961**, 4560.

Generally, one molar DBBS was added into a stirred solution of two molar olefin and six molar 99% formic acid in chloroform under cooling. After the filtration of the separated crystals of benzenesulfonamide, the filtrate was rectificated *in vacuo* to obtain the product. Cyclohexene, styrene, *trans*-β-methylstyrene, and 1-hexene were made to react by this procedure to yield *trans*-2-bromocyclohexyl formate (I), 2-bromo-1-phenylethyl formate (II), *erythro*-2-bromo-1-phenylpropyl formate (III), and 1-bromo-2-hexyl formate (IV), respectively as shown in Table I. The formation of the *erythro*-adduct, III, indicates the *trans*-addition of formate ion on the intermediary bromonium ion. To make sure the orientation of the addition on 1-hexene, 1-bromo-2-hexanol (V)[9] whose formate was identified with IV was oxidized. The spectral data of the product were reasonable to give it the structure of 1-bromo-2-hexanone.

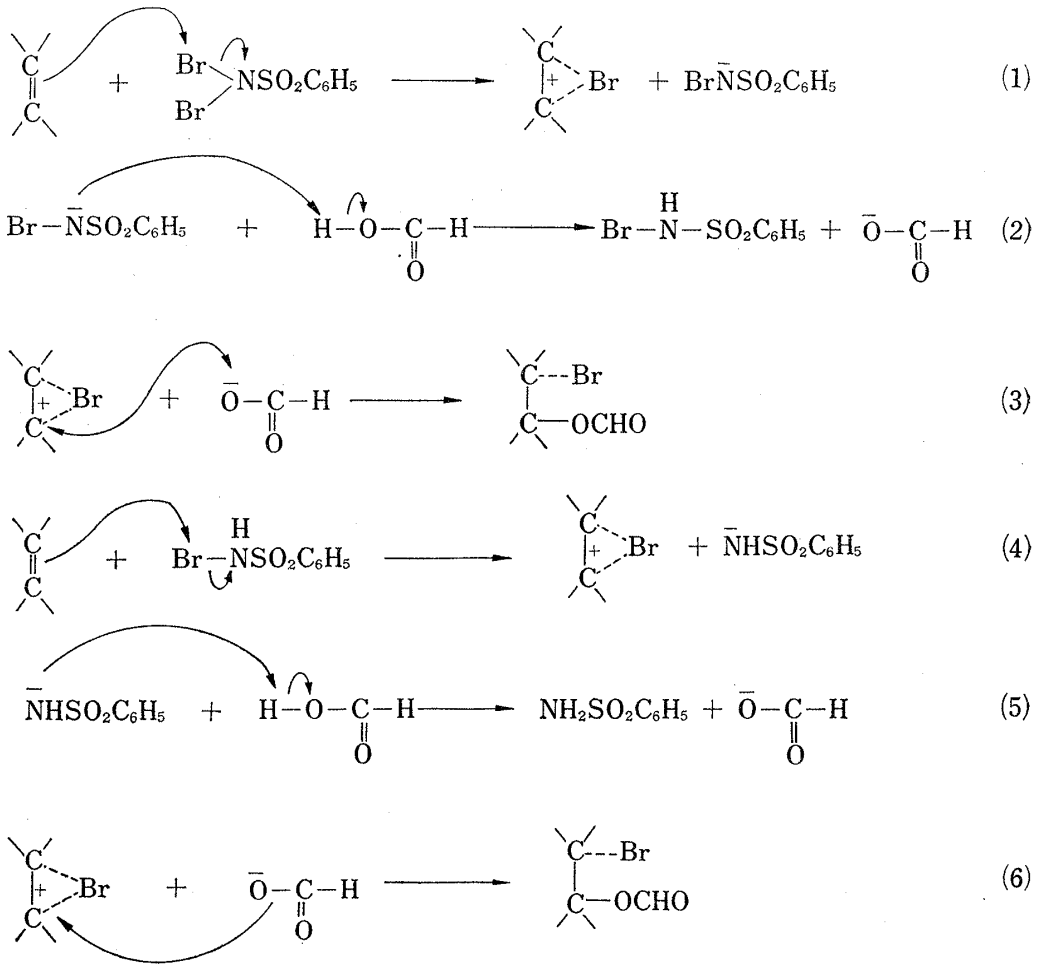


Chart 1

The reaction may be accounted for by a mechanism shown in Chart 1, *i.e.*, addition of Br^+ provided by DBBS to olefin results an intermediate, bromonium ion (Eq. 1), besides the bromosulfonium ion which may accelerate the dissociation of formic acid to formate ion (Eq. 2) and the anion may attack the bromonium ion to form *trans*-β-bromo-formate (Eq. 3), another bromine atom on the sulfonamide recurres similar stage (Eq. 4) and finally benzenesulfonamide and β-bromo-formate are formed (Eq. 5, 6).

9) A. Walti, *J. Am. Chem. Soc.*, **56**, 2725 (1934). No definite proof on the orientation of groups has been given.

Experimental

General Procedure——DBBS (9.4 g, 0.03 mole) was added in small portions into a stirring mixture of olefin (0.06 mole), 99% formic acid (0.18 mole), and $CHCl_3$ (20 ml), in the period of 15 min under cooling with water. After the addition of the reagent was completed, the mixture was stirred for 45 min at room temperature. The separated crystals of benzenesulfonamide were filtered, and washed with $CHCl_3$. The combined $CHCl_3$ solution was washed with three portions of H_2O (5 ml), dried over $CaCl_2$, and evaporated to leave the crude product.

***trans*-2-Bromo-1-cyclohexyl Formate (I)**——The crude product obtained by the reaction of DBBS and formic acid with cyclohexene (6.1 ml) was distilled *in vacuo* to obtain an oil, bp_5 79—86°, n_D^{20} 1.4996 (8.5 g, 68%). It was identified with authentic sample[3] by comparison of infrared (IR) spectra, *Rf* of thin-layer chromatogram, and retention times in gas chromatography.

2-Bromo-1-phenylethyl Formate (II)——The crude product obtained by the reaction with styrene (6.8 ml) in the given general procedure was distilled to give an oil, bp_6 111—113°, n_D^{20} 1.5510 (8.8 g, 65%). It was identical with authentic sample[5] by comparison of IR spectra and *Rf* of thin-layer chromatogram.

***erythro*-2-Bromo-1-phenylpropyl Formate (III)**——The crude product obtained from *trans*-β-methyl-sryrene (7.1 g) in above mentioned general procedure was distilled under reduced pressure to give an oil of bp_7 115—121°, n_D^{23} 1.5420 (10.9 g, 74%). It was identified with an authentic sample[5] by comparison of IR spectra and *Rf* of thin-layer chromatogram.

1-Bromo-2-hexyl Formate (IV)——1) 1-Hexene (5 g) was made to react by the manner described in the general procedure. The crude product was rectificated *in vacuo* to give an oil, bp_5 66—69°, n_D^{21} 1.4585 (7.4 g, 59%). It was identical with formate of V obtained by the following manner by comparison of IR spectra and retention times in gas chromatography. *Anal.* Calcd. for $C_7H_{13}O_2Br$: C, 40.21; H, 6.27. Found: C, 40.18; H, 6.26. IR $\nu_{max}^{liq.}$ cm^{-1}: 1726 ($\nu_{C=O}$), 1165 (ν_{C-O-C}). NMR (ppm): 8.08 (1H, singlet, -OCOH), 5.12 (1H, multiplet, -C<u>H</u>-OCOH), 3.49 (2H, doublet, $J=5$ cps, -C<u>H</u>$_2$Br).
(7.4 g, 59%).

2) A mixture of 99% formic acid (0.3 ml) and Ac_2O (0.2 ml) was dropwise added to 1-bromo-2-hexanol[9] (V) (0.27 g). The mixture was warmed on a water bath for 1 hr. After cooling, H_2O was added, and the separated oil was extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, and the solvent was removed by distillation. The residual oil was distilled *in vacuo* to obtain an oil, bp_4 64°, 150 mg. The oil was purified by passing through a short column of silica gel, followed by the elution with 5% $CHCl_3$ in CCl_4. Evaporation of the solvent of the eluate leaved an oil which was identified with IV synthesized by another route by comparison of IR spectra and retention times of gas chromatography.

Oxidation of V——The oxidation of V was carried out by the method presented by Conant, and Quayle[10] to give an oil, bp_8 65—66°, n_D^{21} 1.4624 (41%). *Anal.* Calcd. for $C_6H_{11}OBr$: C, 40.24; H, 6.19. Found: C, 40.73; H, 6.04. IR $\nu_{max}^{liq.}$ cm^{-1}: 1718 ($\nu_{C=O}$). NMR (ppm): 3.89 (2H, singlet, -CH_2Br), 2.61 (2H, triplet, $J=7$ cps, -C<u>H</u>$_2$-CO-).

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10) J.B. Conant and O.R. Quayle, "Org. Synth.," Coll. Vol. 1, 1956, p. 211.