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Microdetermination of Olefinic Linkage by *N*-Bromosuccinimide

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Synopsis. A simple, accurate, and relatively rapid procedure for the estimation of olefinic linkage with *N*-bromosuccinimide has been presented.

Numerous methods have been developed for the determination of carbon to carbon unsaturation.[1] One of the problems is the development of a method for the determination of olefinic unsaturation, and the wide variation in reactivity of this group in different environments has resulted in the publication of some 3000 analytical methods to cover the whole range of olefinic compounds.[2] The halogenation methods are the most generally employed procedures for the determination of unsaturation in known compounds as well as mixtures. While standard bromine solution is a convenient and relatively stable reagent in macro scale analysis, yet its adaptation to the micro scale is difficult because 0.01 M bromine deteriorates rapidly.[3a]

It is now shown that *N*-bromosuccinimide (NBS) is stable, reactive, and convenient for routine microdetermination of olefinic linkage. The reaction with NBS is at least twenty five times faster than that with bromine.[4] An excess amount of a 1% aqueous solution of NBS is added to the unsaturated organic compound (2—4 mg) in glacial acetic acid at room temperature and kept for 10 min. Excess of NBS is determined titrimetrically against standard sodium thiosulphate. The results are given in Table 1 and are shown to be quite satisfactory (mean error ±0.3%). The present procedure is simple, accurate and relatively rapid for the estimation of olefinic linkage.

It should be noted, however, that (a) none of the procedures described in the literature is applicable to all types of compounds containing the alkene function, and (b) a method yielding consistently reproducible results does not necessarily give the true unsaturation values of the substance under investigation.[3b] Estimation of tetraphenylethylene with NBS gives zero result and the starting material is recovered unchanged. This may be attributed to the absence of hydrogen atoms in the olefinic linkage. The nature of the *para*-substituent in the 1,1-diarylethylenes Ia—g has an influence on their reaction with NBS. In the presence of *para*-alkoxy groups Ia—c the corresponding 2-bromo-

TABLE 1. MICRODETERMINATION OF OLEFINIC LINKAGE BY NBS

Compound	Weight of sample (mg)		Calcd $>$C=C$<$	Found $>$C=C$<$		% error	
Cinnamic acid	2.985	2.395	16.20	16.17	16.00	−0.03	−0.20
	2.715	2.200		16.09	16.40	−0.11	+0.20
	3.430	2.900		16.30	16.50	+0.10	+0.30
Cinnamyl alcohol	2.580	2.655	17.90	18.00	17.60	+0.10	−0.30
	2.900	3.210		18.20	17.80	+0.30	−0.10
Stilbene	1.890	2.000	13.30	13.00	13.50	−0.30	+0.20
	3.150	2.515		13.09	13.20	−0.21	−0.10
	2.550			13.60		+0.30	
Styrene	2.890	3.150	23.06	23.20	22.90	+0.14	−0.16
	2.950	3.810		23.09	22.90	+0.03	−0.16
p-Bromostyrene	2.050	1.815	12.90	13.08	12.85	+0.18	−0.05
	3.805			12.60		−0.30	
Diphenylethylene	2.070	2.370	13.30	13.20	13.00	−0.10	−0.30
	1.135			13.00		−0.30	
Triphenylethylene	4.055	3.200	9.20	9.00	8.99	−0.20	−0.21
	2.545	2.725		9.09	9.10	−0.11	−0.10
	3.050			9.50		+0.30	
2-Bromo-1,1-diphenylethylene	2.015	3.090	9.20	9.00	8.90	−0.20	−0.30
	4.010	3.250		8.90	9.10	−0.30	−0.10
1,1-Bis(*p*-bromophenyl)ethylene	1.830	2.280	7.10	7.30	7.20	+0.20	+0.10
	2.180	1.936		7.00	7.15	−0.10	+0.05
1,1-Bis(*p*-chlorophenyl)ethylene	2.450	3.010	9.60	9.50	9.30	−0.10	−0.30
	2.350			9.80		−0.20	
1,1-Bis(*p*-tolyl)ethylene	1.440	1.925	11.53	11.50	11.40	−0.03	−0.13
	1.680	2.132		11.60	11.40	+0.07	−0.13

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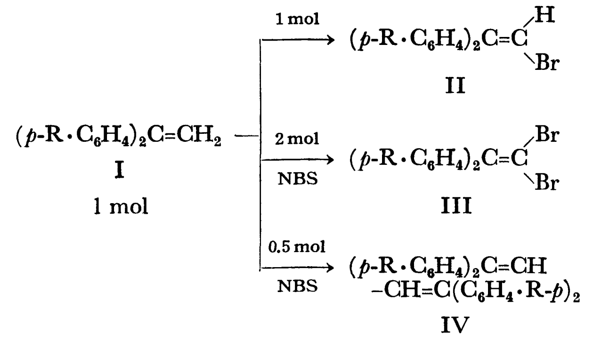
Table 2. Reactions of 1,1-diarylethylenes with NBS

	(I, 0.01 mol) R	NBS mol	II %	II Mp (°C)	III %	III Mp (°C)	IV %	IV Mp (°C)
a	MeO[6)]	0.01	99.6	48[6)]	—	—	—	—
		0.02	—	—	99.3	91[6)]	—	—
		0.005	—	—	—	—	1000	204[7)]
b	EtO[8)]	0.01	99.5	64[8)]	—	—	—	—
		0.02	—	—	99.5	118[6)]	—	—
		0.005	—	—	—	—	100	207[8)]
c	*i*-PrO[8)]	0.01	99.55	52[8)]	—	—	—	—
		0.02	—	—	99.56	62[a)]	—	—
		0.005	—	—	—	—	100	187[9)]
d	H[10)]	0.01	99	42[10)]	—	—	—	—
		0.02	99.2		—	—	—	—
e	Me[11)]	0.01	99.3	64[11)]	—	—	—	—
		0.02	99.6		—	—	—	—
f	Br[12)]	0.01	99.5	104[13)]	—	—	—	—
		0.02	99.5		—	—	—	—
g	Cl[14)]	0.01	99.4	71[13)]	—	—	—	—
		0.02	99.4		—	—	—	—

Reaction period 10 min. Solvent in all experiments, chloroform, 15 ml.

a) Found: C, 52.70; H, 4.80; Br, 35.30%. Calcd for $C_{20}H_{22}Br_2O_2$: C, 52.85; H, 4.84; Br, 35.24%.

ethylene IIa—c, 2,2-dibromoethylene IIIa—c and 1,1,4,4-tetra-arylbuta-1,3-diene IVa—c are isolated with equimolecular, dimolecular, and half-molecular quantities of NBS respectively.



	a	b	c	d	e	f	g
R:	MeO	EtO	*i*-PrO	H	Me	Br	Cl

The mechanism of formation of 1,1,4,4-tetra-arylbuta-1,3-dienes IVa—c is apparently the same as previously described.[5)] On the other hand, the other compounds Id—g gave 2-bromoethylenes IId—g as the only product (Tables 1 and 2).

Experimental

Procedure. Introduce an exactly weighed amount (2—4 mg) of the olefinic compound in a 50 ml Erlenmeyer flask charged with 4 ml of glacial acetic acid. Stirr until the organic compound is dissolved. Add accurately 1 ml of a 1% (w/v) aqueous solution of *N*-bromosuccinimide. The flask is stoppered, shaken and left in the dark for 10 min. Add 4 ml of 10% potassium iodide and titrate the liberated iodine with standard sodium thiosulphate solution (0.02 N) to the starch end-point.

The olefinic linkage is determined by the following equation:

$$\% \; {>}C{=}C{<} = \frac{(a-b)(\text{normality of } Na_2S_2O_3)(24.02)(100)}{(\text{weight of sample in mg})(2)}$$

a = ml of $Na_2S_2O_3$ for blank, and
b = ml of $Na_2S_2O_3$ for sample.

Reactions of 1,1-Diarylethylenes Ia—g with NBS: This is exemplified by the following:

A solution of 1,1-bis(*p*-methoxyphenyl) ethylene[6)] (Ia, 2.4 g, 0.01 mol) in chloroform (15 ml) and NBS (1.78 g, 0.01 mol) in the same solvent (15 ml) was heated to boiling for 10 min. The residue obtained after removal of the solvent was washed with water and then crystallised from 95% ethanol to give 2-bromo-1,1-bis(*p*-methoxyphenyl)ethylene IIa (3.15 g) with mp and mixed[6)] mp 84 °C.

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