The Photobromination of (+)-1-Cyano-2-methylbutane

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The photobromination of (\pm) -1-cyano-2-methylbutane with molecular bromine, under varying conditions, yields a mixture of three monobrominated products: 1-cyano-1-bromo-2-methylbutane (relative yield 78–95%), 1-cyano-3-bromo-2-methylbutane (relative yield 1–5%), and 1-cyano-2-bromo-2-methylbutane (relative yield 4–17%). The production of the major monobrominated product is proposed to arise by an acid catalyzed ionic reaction. When the bromination of (+)-1-cyano-2-methylbutane was carried out in the presence of solid *N*-bromosuccinimide as well as molecular bromine, the three monobrominated products were formed in relative yields that reflected a free radical bromination reaction: (+)-1-cyano-1-bromo-2-methylbutane (5–14%), (\pm) -1-cyano-2-methylbutane (68–85%), and (+)-1-cyano-3-bromo-2-methylbutane (10–19%).

The inability to obtain active 1-cyano-2-bromo-2-methylbutane from these bromination reactions may not be due to the fundamental nature of the bromination of a substrate at a chiral center but may be due to the instability of this particular tertiary bromide.

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La photobromination du (\pm) -cyano-1 méthyl-2 butane avec du brome moléculaire sous diverses conditions conduit à un mélange de trois produits monobromés: le cyano-1 bromo-1 méthyl-2 butane (rendement relatif 78 à 95%), cyano-1 bromo-3 méthyl-2 butane (rendement relatif 1–5%), et cyano-1 bromo-2 méthyl-2 butane (rendement relatif 4–17%). On suggère que la formation prépondérante du produit monobromé majeur provient d'une réaction ionique acido-catalysée. Quand la bromuration du (+)-cyano-1 méthyl-2 butane est effectuée en présence de N-bromosuccinimide de solide en même temps que du brome moléculaire, les trois produits monobromés se forment avec des rendements relatifs qui réflètent une réaction de bromuration radicalique; (+)-cyano-1 bromo-1 méthyl-2 butane (5–14%) (\pm)-cyano-1 bromo-2 méthyl-2 butane (68–85%) et (+)-cyano-1 bromo-3 méthyl-2 butane (10–19%).

Le fait que le cyano-1 bromo-2 méthyl-2 butane est obtenu inactif lors de ces réactions de bromuration peut être du à la nature fondamentale de la bromuration d'un substrat ayant un centre chiral, mais elle peut aussi être du à l'instabilité de ce type particulier de bromure tertiaire. [Traduit par le journal]

Introduction

The formation of free radicals at asymmetric centers by hydrogen abstraction generally leads, after their transfer reactions, to optically inactive products (1, 2). Exceptions to this generalization are the bromination by a number of free radical brominating agents (*viz.*, *t*-butyl hypobromite (3), *N*-bromosuccinimide (4), and molecular bromine (2, 3)) of (+)-1-chloro-2-methylbutane (3) and (+)-1-bromo-2-methylbutane (2–4).

The retention of activity by the brominated products has been attributed to the formation of an intermediate halogen bridged radical, i. The formation of this bridged species was presumed to occur by the assisted removal of the tertiary hydrogen atom by the neighboring halogen atom (5, 6).

It has been suggested that this picture of the bromination pathway has several limitations.

When the active bromide was brominated and the starting material was reisolated after the reaction, it was found that the starting bromide had racemized to a small extent (2). The principle of microscopic reversibility demands that racemization of the starting material (6-14%) of the radicals formed) must arise from the formation of an open radical, which then undergoes rotation, closes again to a bridged radical, and transfers with hydrogen bromide. It was suggested that this sequence of reactions, although possible, was highly unlikely (2). The structure of the intermediate β -bromo and -chloro radicals have, likewise, been modified since both the e.s.r. spectra of the radicals themselves (7–9), or the CIDNP spectra of their transfer products (10), have shown them not to be symmetrically bridged and it has been suggested that a better representation of these intermediates is a partially bridged strucTANNER ET AL.: PHOTOBROMINATION



ture, **ii** (9), or a hyperconjugatively frozen structure, **iii** (7, 8).



An alternative to the bridged structure has been proposed to explain the stereochemical results obtained from the liquid phase photobromination of (+)-1-cyano-2-methylbutane to yield (+)-1cyano-2-bromo-2-methylbutane. It was suggested by the authors (11) that, under the high concentration of bromine necessary for the observation of the retention of optical activity in the three 1-substituted-2-methylbutanes which have been studied, the abstracting species was, in fact, the Br_3 . radical rather than the bromine atom and that upon abstraction both molecular bromine and an alkyl radical are formed as a geminate pair. Accordingly, the retention of activity was due to a rapid cage reaction between them which was faster than the molecular rotation of the radical (11).



It was subsequently pointed out (2) that a bridged cyano group was not as unlikely as Haag and Heiba (11) had first proposed and that there was considerable precedent for considering such an intermediate. An anomaly was also commented on: that the sign of the rotation of the (+)-bromocyanide, contrary to what was reported, would be predicted by Brewster's rules (12) to be inverted to a (-)-bromocyanide if the conversion had taken place with a retention of absolute configuration.¹

Discussion and Results

The photoinitiated reaction of 1-cyano-2methylbutane (1) with molecular bromine (2:1 or 10:1) yielded three monobromination products, 1-cyano-1-bromo-2-methylbutane (2), 1cyano-2-bromo-2-methylbutane (3), and 1-cyano-3-bromo-2-methylbutane (4). Contrary to the



previous study (11), where only 3 was reported, the major isomeric monobromide obtained from the bromination was 1-cyano-1-bromo-2-methylbutane (2), 95%. The minor isomers 3 and 4 were formed in a relative yield of 4 and 1%, respectively. The absolute yields of the three monobromides were low and ranged from 71% at 2:1 (RCN:Br₂) to 57% at 10:1 (RCN:Br₂) ratios of substrate to bromine.

It was apparent from the isomer distribution obtained from the bromination of 1 with molecular bromine that a radical bromination was not leading to the production of the major product 2, since the expected product of radical bromination would result from the substitution of the tertiary hydrogen. A likely explanation for the formation of 2 was an acid-catalyzed α -bromination of the methylene position adjacent to the activating cyano group. The ionic bromination was not found to be extremely rapid under the conditions employed (>0.5-2 days).

The ionic bromination could be greatly minimized by the addition of solid *N*-bromosuccinimide (NBS) to the reaction mixture. The NBS functions as a source of molecular bromine which forms by the reaction of the hydrogen bromide produced in the reaction with the NBS. Photobromination of 1 using mixtures of solid NBS and bromine in carbon tetrachloride (RCN: Br_2 :

2243

¹It is recognized, however, that a molecule with two polar groups on adjacent carbon atoms may exhibit strong dipolar interactions or solvent interactions favoring or disfavoring a particular conformation and the observed rotation may be quite different from what is predicted. When the magnitude of the rotation is small, even an inversion of sign may be observed.



NBS, 6:1:5) gave a 29% yield of the three monobrominated products in the ratio of 2:3:4 of 5:85:10, when the reaction was carried out so that 60.2% of the active bromine was consumed. This method of bromination was, in fact, similar to the method used by Haag and Heiba in their original report (11) of the bromination of (+)-1-cyano-2-methylbutane.²

The two chiral isomeric monobromides (+)-1-cyano-3-bromo-2-methylbutane and (+)-1-cyano-1-bromo-2-methylbutane which are formed in minor amounts during the bromine– NBS brominations were synthesized by independent reactions and isolated by preparative g.l.p.c.

Since the mechanism of the *t*-butyl hypobromite bromination of alkanes proceeds by a free radical chain, carried by the less selective (relative to bromine) t-butoxy radical (13), it was anticipated that a more random distribution of products would be obtained from its use as the reagent for brominating (+)-1-cyano-2-methylbutane. The bromination of (+)-1-cyano-2-methylbutane with t-butyl hypobromite (2:1 mol ratio) yielded upon g.l.p.c. analysis five monobrominated products in the ratio of 19:32:39:4:6. The compounds corresponding to the first two peaks were (+)-1cyano-1-bromo-2-methylbutane and presumably the inactive 1-cyano-2-bromo-2-methylbutane. The compound corresponding to peak 3 was (+)-1-cyano-3-bromo-2-methylbutane ($[\alpha]_{546}^{26}$ +9.40).

The chiral monobromide, (+)-1-cyano-1bromo-2-methylbutane, was synthesized from (+)-1-cyano-2-methylbutane ($[\alpha]_{546}^{24} + 8.97$) with phosphorus tribromide and bromine and was found to have a rotation of ($[\alpha]_{546}^{27} + 6.62$).

The photoinitiated bromination of (+)-1cyano-2-methylbutane with mixtures of molecular bromine and NBS was carried out in the same manner as the bromination of the racemic mixture of that cyanide. Fractional distillation of the product mixture, after the destruction of the excess brominating agent, yielded unreacted starting material (37-40°/8 mm) and a fraction boiling at 52-53°/1 mm. Gas-liquid partition chromatography analysis of this fraction showed it to be primarily 1-cyano-2-bromo-2-methylbutane. The reisolated starting material was purified by preparative g.l.p.c. and was found to be racemized 3-4%. The fraction containing 1cyano-2-bromo-2-methylbutane was redistilled using a 10 in. Vigreux column and a fraction boiling at 48-49°/1.2 mm was collected. Gasliquid partition chromatography analysis of this fraction showed the presence of small amounts of (+)-1-cyano-1-bromo-2-methylbutane (1.4%) and (+)-1-cyano-3-bromo-2-methylbutane (7.0%) as well as the desired 2-brominated isomer.

No attempt was made to isolate the tertiary bromide from the reaction mixture by preparative g.l.p.c. since the attempted isolation of (-)-1,2-dibromo-2-methylbutane in this manner led to extensive racemization, while distillation allowed its isolation (2). Furthermore, g.l.p.c. treatment of 3 leads to small amounts ($\sim 3\%$) of products resulting from the elimination of hydrogen bromide. The tertiary bromide, (\pm) -1-cyano-2-bromo-2-methylbutane, could be synthesized and obtained as a pure material from the reaction of anhydrous hydrogen bromide and a mixture of 1-cyano-2-methyl-1-butene and 1-cyano-2-methyl-2-butene. The product, 3, was found to be unstable and decomposed, giving off hydrogen bromide, upon standing for several days; however, with some care, it was possible to store the pure material.

A synthetic mixture made up of 1.36%of (+)-1-cyano-1-bromo-2-methylbutane and 6.95% of (+)-1-cyano-3-bromo-2-methylbutane and 91.69% of (±)-1-cyano-2-bromo-2-methylbutane was analyzed by g.l.p.c. The chromatogram of the synthetic mixture was identical to that obtained from an analysis of the redistilled fraction obtained from the bromination of the active cyanide (see Fig. 1).

A comparison of the specific rotation obtained for this fraction with that of the synthetic mixture showed them to be identical; the calculated rotation expected from the synthetic mixture was, likewise, found to be identical to that which was observed (see Table 1).

The conditions used to isolate the tertiary bromocyanide were the same as those used to

²In a private communication with Dr. Heiba, we have been informed that their reactions were carried out with added NBS and solid K_2CO_3 , and that the mention of these additives was inadvertently omitted from their paper and that they were anxious to have this oversight corrected in the literature.

TANNER ET AL.: PHOTOBROMINATION

$[\alpha]_{\lambda}$					
λ (nm)	1 <i>a</i> (at 24°)		Loolated 20	Synthetic mixture ^{<i>d</i>} of $2a$, 3 , and $4a$ (at 26°)	
	Before reaction	After reaction ^b	(at 27°)	Observed	Calcd.
589	+ 7.65	+ 7.40	+0.038	+0.036	+0.038
578	+ 7.98	+ 7.63	+0.039	+0.039	+0.040
546	+ 8.97	+ 8.61	+0.046	+0.048	+0.046
436	+14.83	+14.45	+0.078	+0.077	+0.076
365	+22.40	+21.70	+0.120	+0.122	+0.120

TABLE 1.	Optical rotation of reactants and products in the NBS-Br ₂			
bromination of $(+)$ -1-cyano-2-methylbutane, $1a^a$				

^aAll rotations were obtained in carbon tetrachloride. ^bRecovered material had racemized 3-4%, ^cThe isolated material was contaminated with 1.4% of 2a and 7.0% of 4a, see Fig. 1. ^dA synthetic mixture 1.36% of 2a, 91.69% of 3, and 6.95% of 4a. The calculated rotations were obtained using values for 2a and 4a listed in Table 2.



FIG. 1. The g.l.p.c. chromatogram of an isolated fraction of 3 from the bromination (NBS-Br₂) of 1a compared to the chromatogram of a synthetic mixture of 3 and added 2a and 4a: reaction mixture, dark line; synthetic mixture, heavy line.

isolate active (-)-1,2-dibromo-2-methylbutane, without racemization (2). Since the bromination of (+)-1-cyano-2-methylbutane produced minor amounts of two other (+)-chiral monobromides, which could not be removed by distillation, and since the impurities which contaminated the isolated 1-cyano-2-bromo-2-methylbutane accounted for the entire observed rotation of the reaction mixture; we are forced to the conclusion that, in our hands, the bromination of (+)-1cyano-2-methylbutane leads to inactive (\pm) -1cyano-2-bromo-2-methylbutane.

Our observation may not be due to the fundamental nature of the bromination of a substrate at a chiral center, but may very well be due to the instability of this particular tertiary bromide (3).

Experimental

Bromine was washed with concentrated sulfuric acid and distilled from phosphorus pentoxide before use. *N*-Bromosuccinimide (>97% pure by iodometric titra-tion); (-)-2-methybutanol, $[\alpha]_{546}^{27}$ - 6.55 (Aldrich Chemical Company, Inc.); trichlorofluoromethane (Freon 11); and spectroanalyzed carbon tetrachloride (Fisher Scientific Company) were used without further purification.

Instruments

Materials

Preparative g.l.p.c. was carried out on a Hewlett Packard HP-402 all-glass system gas chromatograph and an Aerograph 202 using a 10 ft \times 1/4 in. glass column packed with 10% Carbowax 20M TPA or 10% DEGS on 60-80 mesh Chromosorb P AW. Gas-liquid partition chromatography analyses of product ratios were carried out on an Aerograph HY-FI 600 D (10 ft \times 1/8 in. glass column) and an Aerograph 202 (10 ft \times 1/4 in. glass column) instruments using isothermal conditions. Rotations were recorded on a Perkin-Elmer 141 automatic polarimeter.

(+)-1-Cyano-2-methylbutane (1a)

The active cyanide was prepared by the treatment of the p-toluene sulfonate ester of (-)-2-methylbutanol $([\alpha]_{546}^{27} - 6.55)$ (2) with potassium cyanide.

The tosylate (60 g, 0.25 mol) and a solution of potassium cyanide (86 g, 1.32 mol) in diethylene glycol (80 g) was heated at reflux for 3 h. Fractional distillation of the product mixture yielded 18 g (72%) of pure (+)-1-cyano-2-methylbutane, b.p. $152-154^{\circ}/699$ mm (lit. (14) b.p. $151.4-152.6^{\circ}/743$ mm), n_D^{23} 1.4075 (lit. (14) n_D^{25} 1.4070). The specific rotation of the active cyanide (CCl₄) is listed in Table 2 (lit. (11) $[\alpha]_{548,1}$ + 7.98). The optical rotation of 1a after reisolation by g.l.p.c. gave the same rotation; i.r. v_{max} (liquid film) 2970 (s), 2940 (s), 2880 (s), 2860 (sh), 2240 (m), 1460 (s), 1425 (m), 1380 (m), 1350 (w), 1345 (w), 1155 (w), and 970 (w) cm⁻¹; n.m.r. τ (CCl₄) 7.77 (2H; d; 2-H), 8.0-8.8 (3H, m, 3- and 4-H), 8.93 (3H, d, 3-CH₃), and 9.06 (3H, t, 5-H).

Anal. Calcd. for C₆H₁₁N: C, 74.17; H, 11.41. Found: C, 74.08; H, 11.21.

TABLE 2. Specific rotation of (+)-1-cyano-2-methylbutane (1a), (+)-1-cyano-1-bromo-2-methylbutane (2a), and (+)-1-cyano-3-bromo-2-methylbutane (4a) in CCl₄

2	[α] _λ				
(nm)	1a (at 24°)	2 <i>a</i> (at 27°)	4 <i>a</i> (at 26°)		
589	+ 7.65	+ 5.64	+ 7.88		
578	+ 7.98	+ 5.89	+ 8.18		
546	+ 8.97	+ 6.62	+ 9.40		
436	+14.83	+10.48	+15.85		
365	+22.40	+15.09	+25.21		

1-Cyano-2-methyl-1-butene and

1-Cyano-2-methyl-2-butene

The method of Whyte and Cope (15) was used to synthesize a mixture of these olefins. A benzene solution (150 ml) of methyl ethyl ketone (225 g, 3.1 mol), cyano-acetic acid (245 g, 2.9 mol), glacial acetic acid (90 g, 1.5 mol), and ammonium acetate (46.6 g, 0.6 mol) was heated under a Dean–Stark trap until all of the water had separated. The solvent benzene was removed by distillation and the crude mixture was heated at 145° for 5 h. The reaction products were then distilled at 80 mm. The distillate was washed with water and then dried over anhydrous sodium sulfate. Redistillation gave 149 g (54%) of a mixture of 1-cyano-2-methyl-1-butene and 1-cyano-2-methyl-2-butene, b.p. $82-84^{\circ}/50$ mm; n_D^{23} 1.4396; i.r.

v_{max} (liquid film) 2243 (-CH₂CN), 2220 (-C=CHCN),

1627 (C=C .).

Anal. Calcd. for C₆H₉N: C, 75.74; H, 9.54. Found: C, 75.79; H, 9.64.

(\pm) -1-Cyano-2-bromo-2-methylbutane

Anhydrous hydrogen bromide was bubbled through a stirred solution of 31 g (0.33 mol) of a mixture of 1-cyano-2-methyl-1-butene and 1-cyano-2-methyl-2-butene in 220 ml of ether at 0° for 6 h. The reaction mixture was washed with water, 5% sodium bicarbonate, water, and dried over anhydrous sodium sulfate. Distillation under reduced pressure gave 35.3 g (61%) of (±)-1-cyano-2-bromo-2-methylbutane, b.p. 70.5–71°/5 mm (lit. (16), b.p. 85–86°/13 mm), n_D^{23} 1.4745 (lit. (16) n_D^{22} 1.4772; i.r. v_{max} (liquid film) 2980 (s), 2940 (s), 2920 (sh), 2880 (s), 2840 (sh), 2240 (m), 1455 (s), 1500 (sh), 1430 (m), 1415 (s), 1385 (s), 1345 (w), 1315 (w), 1300 (w), 1285 (w), 1240 (w), 1150 (w), 1115 (s), 1110 (sh), 1088 (m), 1015 (w) cm⁻¹; n.m.r. τ (CCl₄ solution) 7.07 (2H, s, 2-H), 8.05 (2H, q, 4-H), 8.15 (3H, s, 3-CH₃), 8.89 (3H, t, 5-H).

The pure material could be stored for days in the dark at 0° . If left to stand on the bench top for several days it fumed and gave off hydrogen bromide.

Anal. Calcd. for $C_6H_{10}BrN$: C, 40.93; H, 5.72; Br, 45.39; N, 7.96. Found: C, 40.90; H, 5.83; Br, 45.50; N, 7.94.

(+)-1-Cyano-1-bromo-2-methylbutane

A mixture of (+)-1-cyano-2-methylbutane (13.6 g, 0.14 mol), bromine (24.6 g, 0.15 mol), and 2 ml of phosphorus tribromide was heated at 80° for 4 h. The reaction mixture was allowed to cool to room temperature and

then was distilled under reduced pressure (water pump). The distillate was washed with water, 5% sodium bicarbonate, and water again, and dried over anhydrous magnesium sulfate. Redistillation gave 16.3 g (66%) of (+)-1-cyano-1-bromo-2-methylbutane, b.p. 94°/25.5 mm, n_D^{25} 1.4644. The specific rotation is given in Table 1; n.m.r. τ (CCl₄) 5.74 (1H, d, 2-H), 8.70–7.90 (3H, m, 3-and 4-H), 8.82 and 8.79 (3H, d and d, 3-CH₃),³ 8.98 and 9.01 (3H, t and t, 5-H)³; i.r. v_{max} (liquid film) 2238 cm⁻¹ (-C=N).

Anal. Calcd. for $C_6H_{10}BrN$: C. 40.93; H, 5.72; Br, 45.39; N, 7.96. Found: C, 40.61; H, 5.84; Br, 45.53; N, 7.91.

Bromination of (+)-1-Cyano-2-methylbutane with t-Butyl Hypobromite

A mixture (2:1 mol ratio) of (+)-1-cyano-2-methylbutane and t-butyl hypobromite (13) (94% pure by iodometric titration) was sealed in a degassed Pyrex ampoule. The ampoule was thermostated at 25° and irradiated with a 100 W incandescent lamp until colorless (4 h). Gasliquid partition chromatography analysis of the reaction mixture using an Aerograph 202 gas chromatograph equipped with a 1/4 in. \times 10 ft 10% Carbowax 20M TPA on 60-80 mesh Chromosorb P AW glass column (135° isothermal) indicated five monobromo-1-cyano-2-methylbutanes and a small amount ($\sim 5\%$) of a high boiling component, besides t-butyl alcohol and unreacted starting material. Gas chromatography - mass spectral analysis of the reaction mixture showed the first five products to be monobromides. They were present in the following ratio: 19:32:39:4:6. The compounds corresponding to peaks 1, 2, and 3 were isolated by preparative g.l.p.c. using a 1/4 in. \times 10 ft glass column packed with 10% DEGS on Chromosorb P AW. Peaks 1 and 2 were identified as corresponding to 1-cyano-1-bromo-2-methylbutane and 1-cyano-2-bromo-2-methylbutane by a comparison of their g.l.p.c. retention times, and their ¹H n.m.r. and i.r. spectra with those of authentic samples. Nuclear magnetic resonance showed the compound corresponding to peak 3 to be a 1-cyano-3-bromo-2-methylbutane. Its specific rotation is listed in Table 1. ¹H n.m.r. τ (CCl₄) 8.86 and 8.79 (3H, d and d, 3-CH₃),³ 8.29 and

8.26 (3H, d and d, 4-CH₃),³ 8.20–7.70 (1H, m, –CH–), 7.62 and 7.53 (2H, q and q, –CH₂–),³ 5.92 and 5.81 (1H, quintet and octet, –CHBr–); i.r. (in CCl₄) 2245 cm⁻¹ (–C \equiv N).

Anal. Calcd. for $C_6H_{10}BrN$: C, 40.93; H, 5.72; Br, 45.39; N, 7.96. Found: C, 40.99; H, 5.86; Br, 45.36; N, 8.20.

Peaks 4 and 5 corresponded presumably to 1-cyano-2-(bromomethyl)butane and 1-cyano-4-bromo-2-methylbutane. Both of these compounds had parent ions at m/e175 and 177 (C₆H₁₀BrN), 93 and 95 (CH₂Br), and base peak at 55 (C₄H₇).

Photobromination of (\pm) -1-Cyano-2-methylbutane with Molecular Bromine

The brominations were carried out under a helium atmosphere and were isolated from the air by a dioctyl-

³Chemical shifts and couplings that are reported are for the mixture of *erythro* and *threo* isomers.

2246

TANNER ET AL.: PHOTOBROMINATION

Reaction	Mole ratio 1:Br ₂ 2:1	Temperature (°C) 24	Relative yields of monobromides	Yield (%)
1			2 95 3 4 4 1	
2	2:1	40	2 93 3 5 4 2	
3	13:1	24	2 78 3 17 4 5	
4	13:1	40	2 87 3 10 4 3	
5	2:1	25	2 93 3 5.6 4 1.4	66.3 3.8 0.9
6	4.5:1	25	2 90 3 7 4 3	53.1 4.1 1.8
7	10:1	25	2 92 3 6.2 4 1.8	52.4 3.5 1.1

TABLE 3. Bromination of (\pm) -1-cyano-2-methylbutane (1) with molecular bromine

phthalate bubbler (2). Mixtures of (\pm)-1-cyano-2-methylbutane and molecular bromine (under a helium atmosphere) were placed in a thermostated Pyrex water bath and were irradiated using incandescent light. The solution which was stirred continually was irradiated until the bromine color had been discharged. A copious evolution of hydrogen bromide was observed to bubble out through the dioctylphthalate. The reaction mixture was washed with aqueous sodium thiosulfate solution, 5% sodium bicarbonate, and dried over anhydrous sodium sulfate. The reaction mixtures were subjected to g.l.p.c. analysis, using the DEGS column. The major product (>90%)was 1-cyano-1-bromo-2-methylbutane which was isolated and identified by the comparison of its g.l.p.c. retention time, and n.m.r. and i.r. spectra with those of an authentic sample. The minor products, 1-cyano-2-bromo-2-methylbutane and 1-cyano-3-bromo-2-methylbutane, were identified by a comparison of their g.l.p.c. retention times on two columns (DEGS and Carbowax). The conditions used and the relative yields of products are listed in Table 3 (reactions 1-4).

The brominations were repeated in degassed. sealed Pyrex ampoules. The solutions were irradiated until the bromine color was discharged. The tubes were opened and a known amount of chlorobenzene and *o*-dichlorobenzene was added. The reaction mixture was washed with aqueous sodium thiosulfate solution, saturated sodium bicarbonate, and dried over anhydrous sodium sulfate. The solutions were then subjected to g.l.p.c. analysis on the HY-FI g.l.p.c. using a 1/8 in. \times 10 ft glass column packed with 10% Carbowax 20M TPA on 60–80 mesh Chromosorb P AW (135°, isothermal). The absolute yield of the products was obtained (Table 3, reactions 5–7) by using standard calibration curves for the g.c. response of the products and starting material *vs.* chlorobenzene and *o*-dichlorobenzene.

Bromination of (+)-1-Cyano-2-methylbutane (1a) with NBS and Molecular Bromine

The reactions were carried out in degassed, sealed Pyrex ampoules with constant shaking (see Table 4, reactions 1–2) or with continual stirring (see Table 4, reactions 3–6). The thermostated reaction mixtures were irradiated using 2×140 W Hanovia Utility lamps from 68–365 h. At the end of the reaction solid NBS remained in the bottom of the reaction vessel. The reaction solutions were washed with aqueous sodium thiosulfate solution, water, saturated sodium bicarbonate, water again, and dried over anhydrous sodium sulfate, and analyzed by g.l.p.c. using the 1/8 in. \times 10 ft glass column packed with 10% Carbowax 20M TPA. The results and reaction conditions are given in Table 4.

Reaction mixtures (Table 4, 3–6) were distilled under reduced pressure (60 mm) to remove the carbon tetrachloride solvent and the unbrominated starting material (37–40°/8 mm); finally the fraction boiling at 52–53°/1 mm was collected and was found by g.l.p.c. analysis to be primarily 1-cyano-2-bromo-2-methylbutane. This fraction was redistilled and collected at 48–49°/1.2 mm. Gasliquid partition chromatography analysis of the redistilled fraction (48–49°/1.2 mm) showed small amounts of 2a(1.4%) and 4a (7.0%), see Fig. 1. The rotation of this mixture is listed in Table 1. A synthetic mixture of 1.36% of 2a, 6:95% of 4a, and 91.69% of **3** was made and its

CAN. J. CHEM. VOL. 52, 1974

Reactants in CCl ₄					
1a (M)	$\operatorname{Br}_{2}(M)$	NBS (10 ² mol/100 ml)	Reaction No.	Temperature (°C)	Products (2 <i>a</i> :3:4 <i>a</i>)
4.34	0.54	10.9	1 2	25 25	6:80:14 14:68:18
3.73	0.45	9.3	3 4	21 21	10:71:19 12:70:18
2.50	0.32	15.7	5	22	5:80:15
2.23	0.36	16.3	6	33	5:80:10

TABLE 4. Bromination of (+)-1-cyano-2-methylbutane (1a) with NBS and molecular bromine in carbon tetrachloride

observed rotation was compared with that of the material collected by distillation from the reactions, see Table 1. The g.l.p.c. analysis of the synthetic mixture was also compared to this isolated fraction, see Fig. 1.

The reisolated unreacted starting material was purified by preparative g.l.p.c. on a 1/4 in. \times 10 ft glass column packed with 10% Carbowax 20M TPA and its specific rotation was compared to the starting material, 1a, see Table 1.

Small amounts of olefin (<3%) were formed during the analysis of 1-cyano-2-bromo-2-methylbutane. The amount of olefin was found to be variable and was shown to be formed from the decomposition of **3**, since the g.l.p.c. isolated material when reanalyzed still showed a small amount of olefin.

The absolute yield was determined for the reaction (Table 4, reaction 6) by reanalysis of the mixture, after the addition of a known amount of chlorobenzene and a-dichlorobenzene. The extent of reaction was determined by iodometric titration. The reaction mixture was washed with water, sodium bicarbonate solution, again with water, and dried over anhydrous sodium sulfate. The reaction mixture was analyzed by g.l.p.c. (Carbowax 20M TPA) The absolute yield of the three monobromides (Table 4, reaction 6) was found to be 29% based on the active bromine consumed (60%)

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