(18) (a) I. L. Knunyants and V. V. Shokina, *J. Gen. Chem. USSR (Engl. Transl.)*, **25**, 1175 (1955); (b) A. L. Love and R. K. Olsen, *J. Org. Chem.*, **37**, 3431 (1972).
(19) (a) L. Eberson in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, New York, N.Y., 1969, p 53; (b) J. T. Keating and P. S. Skell in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 573; (c) S. D. Ross, M. Finkelstein, and E. J. Rudd, "Anodic Oxidation", Academic Press, New York, N.Y., 1975, p 134.
(20) W. Braun, L. Rajbenback, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).
(21) (a) R. P. Linstead, B. R. Shephard, and B. C. L. Weeden, *J. Chem. Soc.*, 2854 (1951); (b) M. Finkelstein and S. D. Ross, *Tetrahedron*, **28**, 4497 (1972).
(22) (a) T. Iwasaki, H. Horikawa, K. Matsumoto, and M. Miyoshi, unpublished data; (b) L. Eberson and B. Sandberg, *Acta Chem. Scand.*, **20**, 739 (1966).
(23) J. M. Riordan and C. H. Stammer, *Tetrahedron Lett.*, 1247 (1976).
(24) (a) J. E. Barry, M. Finkelstein, E. A. Mayeda, and S. D. Ross, *J. Org. Chem.*, **39**, 2695 (1974); (b) R. R. Rao, S. B. Mulliken, S. L. Robinson, and C. K. Mann, *Anal. Chem.*, **42**, 1076 (1966).
(25) (a) N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966); (b) P. J. Smith and C. K. Mann, *ibid.*, **34**, 316, 1821 (1969).
(26) T. Shono, H. Hamaguchi, and Y. Matsumura, *J. Am. Chem. Soc.*, **97**, 4246 (1975).
(27) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids", Vol. 3, Wiley, New York, N.Y., 1961.
(28) M. Frankel, M. Harnik, and Y. Levin, *J. Am. Chem. Soc.*, **74**, 3873 (1952).
(29) R. K. Olsen, *J. Org. Chem.*, **35**, 1912 (1970).
(30) J. W. Cornforth, *Chem. Penicillin*, 840 (1949); *Chem. Abstr.*, **49**, 2149h (1955).
(31) H. Aoyanagi, H. Okai, S. Ohno, T. Katoh, and N. Izumiya, *Nippon Kagaku Zasshi*, **85**, 656 (1964).
(32) J. M. Davey, A. H. Laird, and J. S. Morley, *J. Chem. Soc.*, 555 (1966).
(33) K. Okumura, T. Iwasaki, T. Okawara, and K. Matsumoto, *Bull. Inst. Chem. Res. Kyoto Univ.*, **50**, 209 (1972).

Reaction of 2,3-Di(*p*-anisyl)-2,3-butanediol with Acetyl Bromide

Yoshiro Ogata,* Atsushi Kawasaki, Michio Haba, and Takayuki Tsujino

Contribution No. 206 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

Received November 2, 1976

The reaction of *meso*-di(*p*-anisyl)-2,3-butanediol (**1**) with acetyl bromide in the presence of a small amount of *N*-phenyl-β-naphthylamine at room temperature is different from the literature,[1,2] and gives *cis*- and *trans*-2,3-di(*p*-anisyl)-2-butene (**6** and **2**) and 2-*p*-anisyl-3-methyl-6-methoxyindene (**5**) together with another isomeric butene, 2,3-di(*p*-anisyl)-1-butene (**7**) and pinacol rearrangement product, 3,3-di(*p*-anisyl)-2-butanone (**4**), but the yield of expected product, 2,3-di(*p*-anisyl)-1,3-butadiene (**3**), is very low. Addition of a small amount of HBr and KI promotes the formation of the butenes with simultaneous decrease in the content of the indene and the butanone. The time–conversion curves for the reaction of **1** and **4** with acetyl bromide were drawn and a mechanism involving dianisyl-3-methylallyl cation (**9**) is suggested.

2,3-Diaryl-1,3-butadiene was reported to be prepared by the dehydration of *meso*-2,3-diaryl-2,3-butanediol with acetyl bromide in the presence of a small amount of *N*-phenyl-β-naphthylamine.[1,2] In the course of our attempt to prepare 2,3-di(*p*-anisyl)-1,3-butadiene (**3**) according to this procedure, however, we found that by long duration of reaction the yield of butadiene **3** was very low and that *trans*-2,3-di(*p*-anisyl)-2-butene (**2**) and 2-*p*-anisyl-3-methyl-6-methoxyindene (**5**) were obtained together with a certain amount of 3,3-di(*p*-anisyl)-2-butanone (**4**) and other products. The easy formation of pinacolone **4** is anticipated under these acidic conditions, because the *p*-anisyl group has a high migratory aptitude in the pinacol rearrangement[3] and the substituted butadiene **3** can be converted to the substituted indene **5** by acid catalysts,[1] but the substituted butene **2** is an unexpected product. We tried to confirm the reaction products and to elucidate the mechanism for this abnormal formation of **2** and other products.

Results and Discussion

When the reaction of pinacol **1** with acetyl bromide in the presence of a little *N*-phenyl-β-naphthylamine was carried out at 0 °C for 2 h according to the literature procedure,[2] the main products were pinacolone **4** and indene **5** together with minor products such as butadiene **3** and butenes **2**, **6**, and **7**, as shown in Table I.

The products were identified by NMR, IR, and MS, and GLC products **2**, **3**, **4**, and **5** were isolated by column chromatography using silicic acid as an adsorbent and benzene–petroleum ether as an eluent. The yields of butenes **2**, **6**, and **7** were low after 2-h reaction at 0 °C (run 1), but at higher temperature (run 2), longer reaction time (run 3) or addition of KI and HBr (runs 4 and 6) caused an increase in the contents of the butenes with a simultaneous decrease in the content of pinacolone **4** and indene **5**. These results suggest that reducing agents such as HBr and HI promote the formation of butenes **2**, **6**, and **7**. Acetyl bromide which can give HBr by the reaction with pinacol **1** is effective in the butene formation and, as expected, acetyl chloride is also effective in the presence of KI (run 9).

Acetic anhydride as well as acetyl chloride as a diluent suppressed the butene formation (runs 7 and 8). The amine acts to increase the amount of butadiene **3** but decreases that of indene **5** (runs 10 and 11). Excess acetyl bromide tends to increase the amount of **5** and pinacolone **4**, but decreases those of other products (runs 2 and 5).

Figure 1 shows the time–conversion curves in the reaction of pinacol **1** with acetyl bromide. Figure 1 implies the initial formation and then gradual consumption of indene **5** and diene **3** to butenes **2**, **6**, and **7**. The total recovery decreases to 70%, probably because of the formation of tarry material; the decrease of indene **5** seems to be parallel to the decrease of whole products.

Since pinacol **1** under these acidic reaction condition can be converted to pinacolone **4** at an early stage of the reaction, the reaction of **4** with acetyl bromide was examined. On addition of acetyl bromide to the pinacolone, the same products and the similar time–conversion curve as Figure 1 were obtained, but the reaction with pinacolone **4** was much slower than pinacol **1**. Hence, the reaction of **1** to give butenes **2**, **6**, and **7** would not proceed mainly via pinacolone **4**. Also, addition to KI to the system of **4**–AcBr accelerated the reaction of pinacolone **4**, giving the butenes **2** and **6**.

Figure 1 might suggest a pathway **1** → **5** → **2**, **6**, and **7**, but it is less plausible, since the treatment of indene **5** with acetyl bromide alone, aqueous HBr, acetic anhydride, or acetyl

Table I. Products Distribution for the Reaction of 2,3-Di(*p*-anisyl)-2,3-butanediol (1) with Acetyl Bromide

	Run, % composition										
Product	1[a]	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8[h]	9[i]	10[j]	11[k]
6	6	25	37	45	4	32	Trace	Trace	11	4	3
2	6	21	32	36	8	51	Trace	Trace	22		
7	2	5	19	11			Trace	Trace		4	1
3	12	4	3	1	1	2	15	20	2	7	18
4 (+1)	51	6	0	1	25	3	72	9	44	61	65
5	24	39	9	6	63	13	13	71	21	22	10

[a] A reaction in an ice bath for 2 h (1, 4 g; AcBr, 12.5 mL; amine, 0.25 g). [b] A reaction of the mixture in footnote *a* in an ice bath for 0.5 h and at ambient temperature (~15 °C) for 1.5 h. [c] A reaction of the mixture in footnote *a* in an ice bath for 0.5 h and at ambient temperature (~15 °C) for 4.5 h. [d] A reaction in an ice bath for 0.5 h (1, 2 g; AcBr, 4 mL; amine 0.13 g; KI, 1.1 g). [e] A reaction in an ice bath for 0.5 h and at ambient temperature for 1 h (~25 °C) (1, 0.5 g; AcBr, 3 mL). [f] A reaction in an ice bath for 5 min and at ambient temperature (~25 °C) for 55 min (1, 0.5 g; AcBr, 4.5 mL; 47% aqueous HBr, 0.5 mL). [g] A reaction at ambient temperature for 2 h (1, 1 g; AcBr, 1 mL; Ac_2O, 4 mL). [h] A reaction at ambient temperature (~25 °C) for 16 h (1, 3 g; AcBr, 15 mL; Ac_2O, 3 mL). [i] A reaction at ambient temperature (~25 °C) for 20 min (1, 0.2 g; AcCl, 2 mL; KI, 0.2 g). [j] A reaction in an ice bath for 2 h (1, 2 g; AcBr, 6.2 mL). [k] A reaction in an ice bath for 2 h (1, 2 g; AcBr, 6.2 mL; amine, 0.65 g).

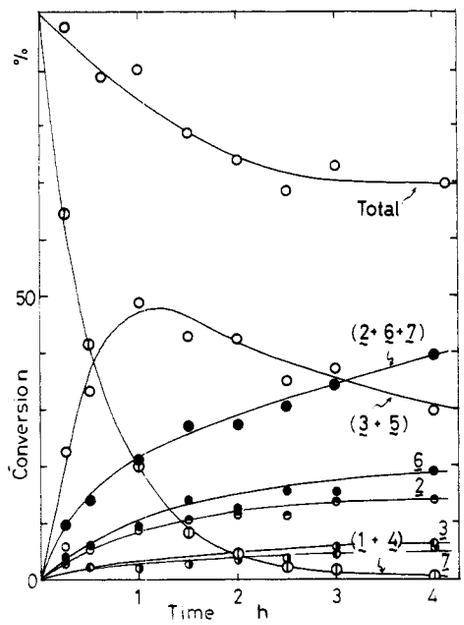
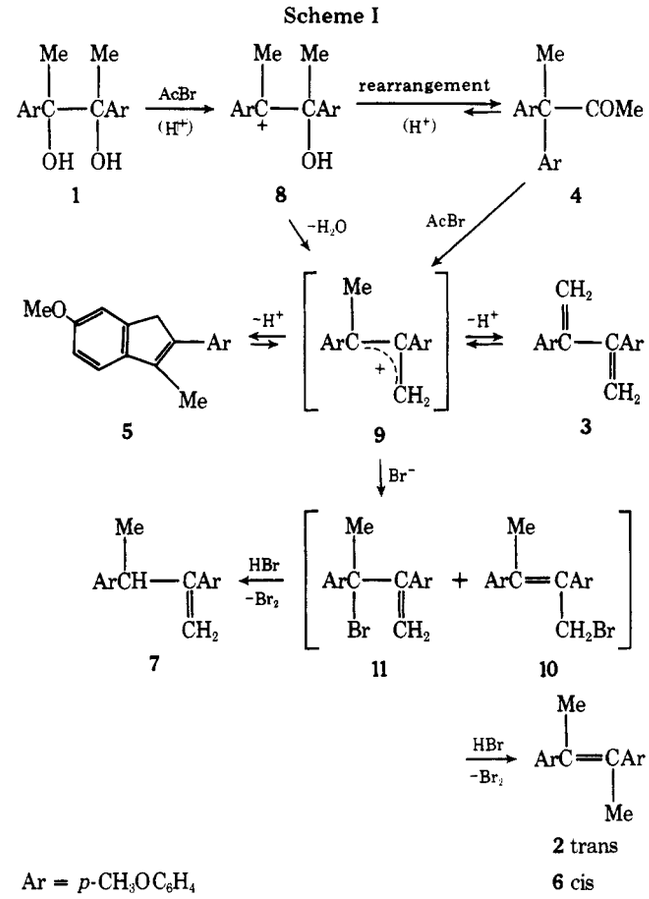


Figure 1. Reaction of pinacol 1 (0.91 g) with acetyl bromide (8.3 g) in the presence of *N*-phenyl-β-naphthylamine (0.03 g) at ambient temperature (~18 °C).

Scheme I



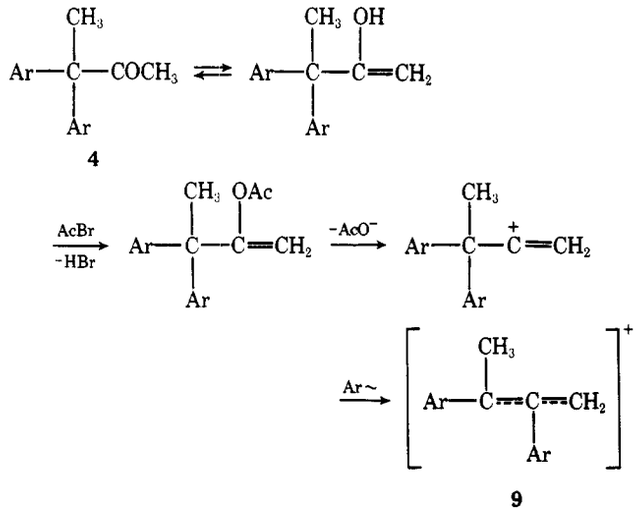
bromide–KI for over 15 h gave only a small amount of butenes **2**, **6**, and **7** with recovery of most of indene **5**. These observations suggest a tentative mechanism of Scheme I for the reaction, where a shorter arrow means the slower rate.

Intermediary carbonium ion **8** is well established in the pinacol rearrangement. Dehydration of this cation leads to allyl cation **9** which may be a key intermediate in this reaction. The scheme is supported by the fact that butadiene **3** reacted with acetyl bromide to give indene **5** (70%) together with butenes **2** (7%) and **6** (3%) with recovery of **3** (21%). A facile acid-catalyzed cyclization of 2,3-diphenyl-1,3-butadiene (**3**, Ar = Ph) to the corresponding indene has been reported.[1]

The observation that pinacolone **4** reacted with difficulty with HBr, but reacted with acetyl bromide to give indene **5** and butenes **2**, **6**, and **7**, suggests that the reaction of **4** proceeds via the enol ester followed by the elimination of acetate ion and rearrangement to give cation **9**.

HBr[4] and HI[5] have been shown to be effective agents for the reduction of olefins, alcohols, and alkyl halides, and these reductions were suggested to proceed via alkyl bromides and iodides.[6] Similarly, the pathway to **2**, **6**, and **7** from **9** probably involves the formation of 1- and 3-butenyl bromides, while a direct hydride transfer from HBr to **9** is inconceivable because of the instability of formed Br^+. Addition of iodide, which is a reducing agents more effective than bromide, promotes the reduction to the butenes.

Since cyclization of cation **9** to **5**, deprotonation to **3**, and reduction to **2**, **6**, and **7** compete with each other, as shown in Scheme I, addition of HBr or KI should favor butenes **2**, **6**, and **7**, but not favor the formation of indene **5** and butadiene **3**, which was found to be the case. The use of acetyl chloride or acetic anhydride as a diluent, which retards the reduction, favors the formation of **5** and **3** as was observed (runs 7 and 8). Detection of molecular bromine by sodium thiosulfate and the monobromo derivative of *N*-phenyl-β-naphthylamine by



GLC–MS (*m/e* 299, 297, and 219) from the products mixture is an additional support to the conversion of HBr to Br_2 in the reaction system.

Another possible mechanism is that involving the reduction of pinacolone **4** with hydrogen bromide to 3,3-di(*p*-anisyl)-2-butanol followed by a retropinacol-type rearrangement to form butenes **2**, **6**, and **7**. This is less plausible, since the pinacolone reacted under similar conditions much slower than the pinacol and does not undergo facile reduction by HBr to the butanol.

$$MeCO{=}CMeAr_2 \xrightarrow{HBr} MeCH(OH){-}CMeAr_2$$

$$\xrightarrow{H^+} MeCH{-}CMeAr_2$$

$$\xrightarrow{\sim Ar} MeCHAr{-}CMeAr \xrightarrow{-H^+} \textbf{2, 6, and 7}$$

In conclusion, pinacol **1** can be easily converted to butenes **2**, **6**, and **7** with an acetyl bromide–KI mixture in one operation. It is preferentially converted to pinacolone **4**, indene **5**, and butadiene **3** with acetyl bromide–acetic anhydride mixture. Indene **5** (mp 112.5 °C) might be wrongly assigned by Sisido et al.[2] the isomeric structure **3** (mp 110 °C) on the basis of its melting point and elemental analysis alone.

Experimental Section

Materials. Butanediol **1** was prepared by the reductive coupling of *p*-methoxyacetophenone with amalgamated aluminum foil in a mixture of absolute ethanol and dry benzene:[2] meso isomer, mp 165–167 °C (lit.[7] 168–169 °C); *dl* isomer, mp 125–127 °C (lit.[7] 122–123 °C). Ketone **4** was prepared according to the literature,[2] mp 72–73 °C (lit.[2] 69–70 °C). Acetyl bromide, bp 74.5–75 °C, acetyl chloride, bp 50–51 °C, acetic anhydride, bp 114–116 °C, and *N*-phenyl-β-naphthylamine were guaranteed grade commercial reagents.

Reaction of Butanediol 1 with Acetyl Bromide. According to the Sisido's procedure,[2] acetyl bromide was added dropwise to a mixture of **1** and *N*-phenyl-β-naphthylamine in a flask equipped with a dropping funnel and a calcium chloride tube with stirring. After reaction at 0 °C for 2 h in an ice bath, the excess acetyl bromide was removed by distillation in vacuo, and then the mixture was poured into cold aqueous Na_2CO_3 (30%). The products were extracted with benzene, dried over $MgSO_4$, and separated by column chromatography with silicic acid using petroleum ether–benzene as a solvent, and determined by GLC on a Yanagimoto GCG-550 F gas chromatograph, employing a flame ionization detector and a 1.0 m × 2.5 mm stainless-steel column packed with silicone OV (5%) on Shimalite or PEG 20 M (2.5 %) on Chamelite CS using N_2 as a carrier gas at 150–280 °C.

The products were identified by IR, NMR, and mass spectra. Mass spectra were recorded on a Shimadzu Model GCMS 7000 mass spectrometer.

***trans*-2-Butene 2,** mp 128.5–130 °C (lit.[2] 126–128 °C), was identified by comparison of the IR spectrum with that of the authentic sample prepared according to ref 2: NMR (CCl_4) τ 8.17 (s, 6 H), 6.2 (s, 6 H), 3.23 (d, 4 H, *J* = 9 Hz), 2.92 (d, 4 H, *J* = 9 Hz); UV λ_{max}^{EtOH} 248 nm (log ε 4.2); mass spectrum *m/e* 268 (M^+), 253, 238. The mass spectrum of **6**, *m/e* 268, 253, and 238, and isomerization of trans-isomer **2** (100%) by iodine catalyst giving an equilibrium mixture of **6** (38%) and **2** (62%) indicate that **6** is a cis isomer of **2**. As shown below, the acid-catalyzed dehydration of 3,3-di(*p*-anisyl)-2-butanol gave **6** together with **2** and **7**, and this also supports the structure assigned for **2** and **6**. The mass spectrum of 1-butene **7** showed *m/e* 268 (M^+), 135, 133. The assignment for **7** is supported by the formation of **7** by dehydration of 3,3-di(*p*-anisyl)-2-butanol.

Butadiene 3: mp 109–110 °C (lit.[2] 108–109 °C); mass spectrum *m/e* 266 (M^+), 251, 236, 133; NMR ($CDCl_3$) τ 6.2 (s, 6 H), 4.67 (d, 2 H, *J* = 1.5 Hz), 4.43 (d, 2 H, *J* = 1.5 Hz), 3.13 (d, 4 H, *J* = 9 Hz), 2.55 (d, 4 H, *J* = 9 Hz).

Pinacolone 4: mp 72–73 °C (lit.[2] 69–70 °C); mass spectrum *m/e* 241 (M^+ CH_3O); IR (cm^{-1}) 1700.

Indene 5: mp 112–112.5 °C; mass spectrum *m/e* 266 (M^+); λ_{max}^{EtOH} 301 nm (log ε 3.98), 270 (log ε 4.2); NMR ($CDCl_3$) τ 7.82 (t, 3 H, *J* = 1.9 Hz), 6.45 (q, 2 H, *J* = 1.9 Hz), 6.27 (s, 6 H), 2.6–3,4 (m, 7 H). The methylene at τ 6.45 has a long-range coupling with methyl at τ 7.82 to afford quartet and triplet, respectively.[8] Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found. C, 80.28; H, 6.76.

Other Reactions of Butanediol 1. In the other runs, acetyl bromide, acetyl chloride, or acetic anhydride–HBr was added at once to a mixture of **1** and other additives. The flask was stoppered and kept standing with occasional shaking for the appropriate length of time.

Time–Conversion Curves for Reaction of Butanediol 1 with Acetyl Bromide. For the time–conversion measurements, aliquots were pipetted out, treated with ice-cold aqueous Na_2CO_3, extracted with benzene, and dried over $MgSO_4$ and then the product contents were determined by GLC analysis using deoxybenzoin as an internal standard. **2** + **6** + **7** means the amount of butene isomers and **3** + **5** means that of isomers of butadienes.

Acid-Catalyzed Dehydration of 3,3-Di(*p*-anisyl)-2-butanol. The alcohol, which was prepared by the reduction of pinacolone **4** (3 g) with Na–EtOH in xylene,[2] was treated with acetic acid (16 mL)–H_2SO_4 (6 mL)–water (13 mL). After 5-h reaction time, a part of the mixture was poured into ice-cold aqueous Na_2CO_3, extracted with ether, and dried over $MgSO_4$. The GLC analysis of the extract showed that the reaction was not completed and it contained a mixture of **6** (22%), **2** (21%), **7** (10%), and unreacted alcohol (47%). After addition of acetic acid (10 mL) and H_2SO_4 (2 mL), the reaction was continued for 3 h. The mixture was treated with cold water and the resulting precipitate was recrystallized from methanol. Pure *trans*-butene **2** was obtained, 1 g (33%), mp 128.5–130 °C (lit.[2] 126–128 °C).

Registry No.—**1**, 62154-11-4; **2**, 17324-35-5; **3**, 52255-88-6; **4**, 22927-05-5; **5**, 62154-12-5; **6**, 54953-13-8; **7**, 15542-00-4; *p*-methoxyacetophenone, 100-06-1; acetyl bromide, 506-96-7; 3,3-di(*p*-anisyl)-2-butanol, 62154-13-6.

References and Notes

(1) C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Res., Sect. B*, **17**, 75, 80, 81 (1939).
(2) K. Sisido, H. Nozaki, and T. Iwako, *J. Am. Chem. Soc.*, **71**, 2037 (1949); K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 776 (1948).
(3) W. E. Bachman, and J. W. Ferguson, *J. Am. Chem. Soc.*, **56**, 2081 (1934).
(4) R. A. Altschul and P. D. Bartlett, *J. Org. Chem.*, **5**, 623 (1940); M. Couper and R. E. Lutz, *ibid.*, **7**, 79 (1942); M. Kobayashi, *J. Chem. Soc., Pure Chem. Sect.*, **69**, 37 (1948).
(5) D. Vorländer and P. Weinstein, *Ber.*, **56**, 1122 (1923); H. Biltz and M. Kohel, *ibid.*, **54**, 1820 (1921); S. L. Shapiro, C. G. Overberger, *J. Am. Chem. Soc.*, **76**, 97 (1954).
(6) M. Kobayashi, *J. Chem. Soc., Jpn., Pure Chem. Sect.*, **74**, 884 (1953); K. Ichikawa and E. Miura, *ibid.*, **74**, 798 (1953).
(7) C. C. Price and G. P. Mueller, *J. Am. Chem. Soc.*, **66**, 634 (1944).
(8) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd ed, Wiley, New York, N.Y., 1974, p 191.