Free-Radical Addition of Hydrogen Bromide to 1-Hexene. Mechanism of Formation of 2-Bromo- and 3-Bromohexanes

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Abstract: A novel double-bond migration is shown to occur during the photolytic addition of hydrogen bromide to 1-hexene in the liquid phase. It is demonstrated that hydrogen bromide catalyzes the isomerization of 1-hexene to 2-hexene, and that subsequent addition of hydrogen bromide to the 2-hexene yields a nearly equimolar mixture of 2-bromohexane and (previously undetected) 3-bromohexane. The product, 2-bromohexane, has usually been attributed to ionic addition. This work shows that the 2-bromo and 3-bromo compounds are formed by a modified free-radical chain reaction.

The addition of hydrogen bromide to an α-olefin is usually represented as a competition between ionic addition to yield 2-bromoalkane, the normal or Markovnikov product, and free-radical chain addition to yield 1-bromoalkane, the abnormal or anti-Markovnikov product.[1-3] Either path may usually be made to predominate under appropriate reaction conditions: *i.e.*, the ionic path is favored at low temperature in polar solvents in the presence of free-radical inhibitors while the radical path is favored at elevated temperatures in the presence of free-radical initiators. It has generally been concluded that the radical addition reaction has a greater temperature coefficient than the ionic addition;[3] however, studies in our laboratories and in the recent literature[4] have demonstrated that the addition of hydrogen bromide to an α-olefin such as 1-hexene yields increasing amounts of 2-bromo-substituted product with increasing temperature. Clippinger suggested that the ionic addition actually has a greater temperature coefficient than the radical addition with α-olefins.[4] The present paper describes a kinetic and product study of the photolytic addition of hydrogen bromide to 1-hexene with the objective of resolving this anomaly.

Experimental Section

Reagents. 1-Hexene (Phillips Pure Grade) was used directly with no purification. Glpc analysis showed that the material was 99.62% pure with the impurity being *cis*- and *trans*-2-hexene (0.38%). Hydrogen bromide (The Matheson Co., Inc., Research Grade) was used directly. The minimum purity is 99.8%.

Kinetic Runs. A 500-ml, four-necked, round-bottomed flask was fitted with a reflux condenser, a sintered glass inlet tube for introducing HBr, a Y tube with a $^1/_8$-in. i.d. Teflon tube for N_2 purge and sample withdrawal and a thermocouple well, and a quartz thimble containing a 100-w GE AH4 light source. A Teflon-covered magnetic stirring bar was used to stir the contents of the flask. In a typical kinetic run, 125 ml of 1-hexene (1.0 mole) was charged to the flask and purged with N_2 for 15 min. The desired temperature was obtained by heating with an electric mantle or cooling in an ice bath. HBr was introduced at a rate of 0.21 mole/hr through a calibrated rotameter. Samples were withdrawn periodically with a hypodermic syringe *via* the Teflon tube. The samples were stored at $-196°$ until analyzed.

Potassium ferrioxalate dosimetry demonstrated that with the above geometry, the photon input from the 100-w lamp is 0.00084 einstein/hr. Sixty per cent of the light has a wavelength <2750 A.

The samples were analyzed by glpc using a 25 ft × 0.25 in. o.d. 20% Ucon P on firebrick column with a helium flow rate of 75 cc/min. The column was maintained at 40° until the olefins had emerged, and then programmed from 40 on 160° at 10°/min. The glpc analysis was calibrated using synthetic mixtures of the various products. The 2-bromo- and 3-bromohexanes were not resolved on the above column. 2-Bromo- and 3-bromohexane were nearly completely resolved on a 200 × 0.01 in. i.d. stainless steel capillary column coated with polyphenyl ether. The column was maintained at 35° for 34 min and then programmed from 35 to 100° at 2°/min.

The *cis*- and *trans*-2-hexenes were identified by comparing the infrared spectra of glpc-trapped samples with the spectra of authentic material in API Research Project 44 selected infrared spectral data. 1-Bromohexane and the mixture of 2-bromo- and 3-bromohexanes were identified by comparing the infrared spectra of glpc-trapped samples with the authentic materials (Eastman Organic Chemicals and Columbia Organic Chemicals Co., Inc., respectively), and by glpc retention times on the capillary column.

Results

The product composition from the ultraviolet light initiated addition of HBr to 1-hexene was studied as a function of time at several temperatures. The reaction conditions, low HBr concentration, source of free-radical initiation, and elevated temperatures (>0°), should favor the free-radical addition. These reaction conditions yielded a minimum quantum yield of 400 for total product formation indicating a long kinetic chain length. The results of three experiments wherein the rates of product formation were measured at 4, 40, and 63.6° are summarized in Figures 1, 2, and 3, respectively. Frequent samples were withdrawn during the first hour of the reaction at 4° to establish the initial rates of formation, and these data are shown in Figure 1a. The conclusions from these data are as follows.

(1) *cis*- and *trans*-2-hexenes are products formed with a finite slope at zero time, and their concentration rises, passes through a maximum, and then falls.

(2) 3-Bromohexane is formed in an amount nearly equivalent to 2-bromohexane. The final product from the addition of HBr to 1-hexene at 4° contains 82.8% 1-bromohexane, 9.9% 2-bromohexane, and 7.3% 3-bromohexane. The addition at 40° yields a product with 70.2% 1-bromohexane, 16.0% 2-bromohexane, and 13.4% 3-bromohexane. The addition at 63.6° yields 53.0% 1-bromohexane, 23.3% 2-bromohexane, and 21.8% 3-bromohexane.

(3) The combined yield of 2- and 3-bromohexanes at complete conversion of the hexenes increases with increasing temperature.

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(1) F. R. Mayo and C. Walling, *Chem. Rev.*, 27, 351 (1940).
(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 7.
(3) F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, 13, 155 (1963).
(4) E. Clippinger, *Ind. Eng. Chem. Prod. Res. Develop.*, 3, 3 (1964).

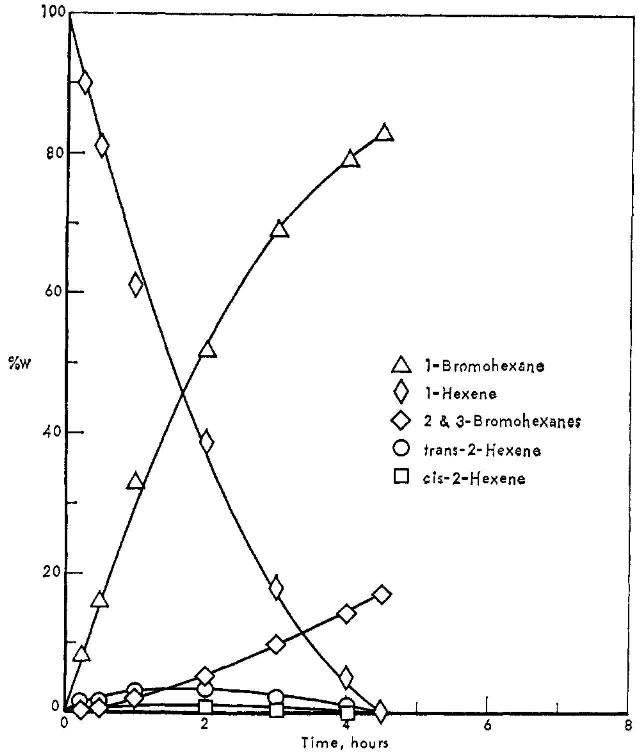

Figure 1. Product composition from addition of HBr to 1-hexene at 4°.

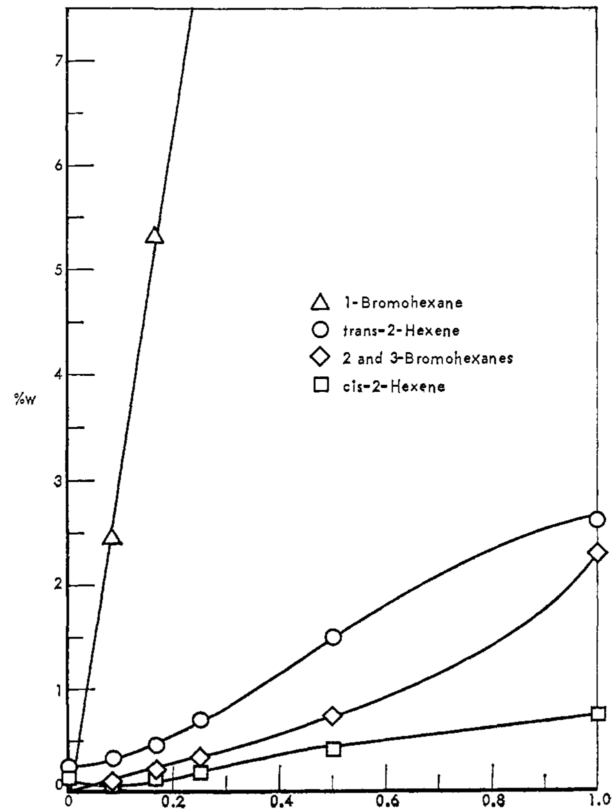

Figure 1a. Initial product composition from addition of HBr to 1-hexene at 4°.

(4) The maximum observed concentration of *cis*- and *trans*-2-hexenes increases with increasing temperature.

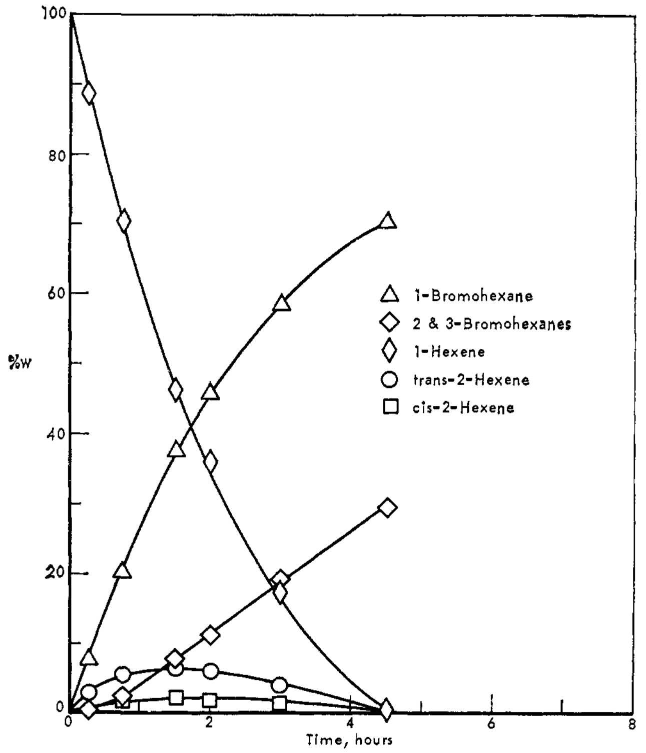

Figure 2. Product composition from addition of HBr to 1-hexene at 40°.

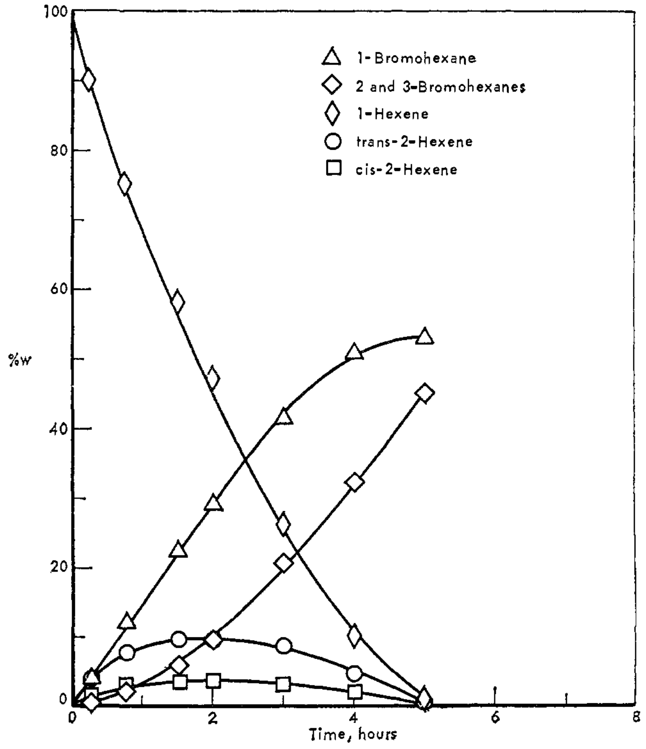

Figure 3. Product composition from addition of HBr to 1-hexene at 63.6°.

(5) The rate of formation of 1-bromohexane is nearly constant at low conversion and seems to be limited by diffusion of HBr. The rate of formation of 2- and 3-bromohexanes is very slow at first and increases with time, and is directly proportional to the concentration of 2-hexenes (Figure 4).

Discussion

Double-Bond Migration. The identification of *cis*- and *trans*-2-hexenes as intermediate products from the free-radical addition of gaseous HBr to 1-hexene in the liquid phase at temperatures as low as 4° is a new result. Previously, Abell had reported that the photolytic addition of HBr to 1-butene in the gas phase at 40–80° was accompanied by isomerization to *cis*- and *trans*-2-butene; however, the mechanism or significance of this isomerization was not discussed.[5] Since completion of the present investigation, Abell has reported the results of a mechanistic study of the double-bond migration of terminal olefins using DBr.[6] Abell obtained evidence for the following radical chain

$$\left.\begin{array}{l} Br\cdot + CH_2{=}CHCH_2CH_3 \rightleftharpoons \\ Br\cdot + CH_3CH{=}CHCH_3 \rightleftharpoons \end{array}\right. \left[\begin{array}{c} CH_2{=}CH\dot{C}HCH_3 \\ \updownarrow \\ \cdot CH_2\dot{C}H{=}CHCH_3 \end{array}\right] + HBr$$

reaction to account for the double bond migration observed during the photolytic addition of HBr to 1-butene in the gas phase. Our results supplement Abell's work and demonstrate that the double-bond migration is a significant reaction in the liquid phase at temperatures as low as 4°.

While it appears possible that the 2-hexene resulting from isomerization of 1-hexene in our study could be further isomerized to 3-hexene by the above mechanism, no 3-hexene was detected in the reaction products.

Formation of 2- and 3-Bromohexanes. The present work demonstrates that 3-bromohexane as well as the expected 2-bromohexane is formed during the free-radical addition of HBr to 1-hexene. The formation of nearly equivalent amounts of 2- and 3-bromohexanes and the detection of *cis*- and *trans*-2-hexenes as intermediate products strongly suggest that both the 2- and 3-bromohexanes are formed by free-radical chain addition of HBr to the 2-olefin.

$$CH_3CH{=}CHC_3H_7 + HBr \xrightarrow{h\nu} \begin{array}{c} CH_3CHBrCH_2C_3H_7 \\ \text{and} \\ CH_3CH_2CHBrC_3H_7 \end{array}$$

The addition of HBr to internal olefins normally leads to a 50:50 mixture of the two possible isomers.[7] In the present study the amount of 2-bromohexane was slightly larger than 3-bromohexane at all temperatures suggesting that ionic addition of HBr to 1-hexene contributes a small fraction of the 2-bromohexane.

The following evidence from the kinetic investigation is additional support for the role of *cis*- and *trans*-2-hexenes as the principal precursors for 2- and 3-bromohexanes. Considering the rates of product formation (see Figures 1–3), it is noted that the initial rate of formation of 2- and 3-bromohexanes has a small (but finite) value near zero time, and that the rate increases with time. This increase in rate suggests that the rate of formation of 2- and 3-bromohexanes is dependent upon the concentration of an intermediate product which is strongly increasing with time. 2-Hexene fulfills this requirement since the rate of formation of 2- and 3-bromohexanes at each temperature studied is directly proportional to the 2-hexene concentration (see Figure 4). The presence of 0.38% 2-hexenes in the starting material and a slow ionic addition to 1-hexene account for the small finite value for the rate of formation of 2- and 3-bromohexanes near zero time.

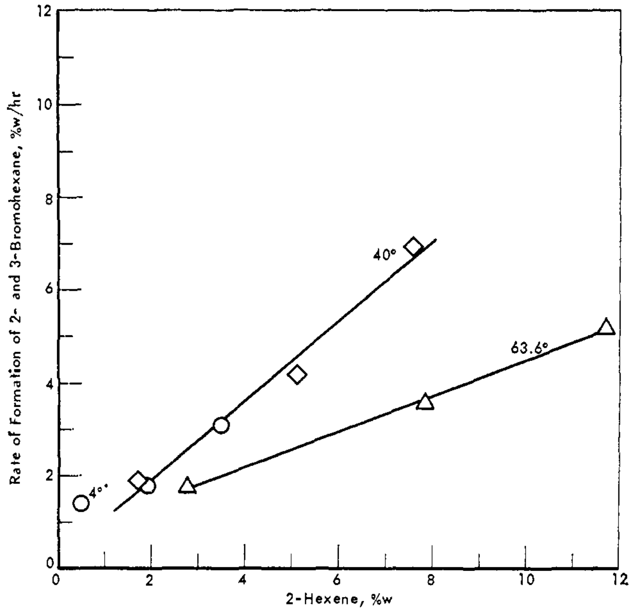

Figure 4. Rate of formation of 2- and 3-bromohexane as a function of 2-hexene concentration: 0 to *ca.* 50% conversion.

Mechanism for Free-Radical Addition of HBr to 1-Hexene. These results indicate that the classical mechanism for the free-radical addition of HBr to 1-hexene should be modified to include reactions 3, 4, and 5 as summarized below.

$$HBr \xrightarrow{h\nu} H\cdot + Br\cdot$$

$$Br\cdot + CH_2{=}CHCH_2C_3H_7 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BrCH_2\dot{C}HCH_2C_3H_7 \qquad (1)$$

$$BrCH_2\dot{C}HCH_2C_3H_7 + HBr \xrightarrow{k_2} BrCH_2CH_2CH_2C_3H_7 + Br\cdot \qquad (2)$$

$$\begin{array}{l} Br\cdot + CH_2{=}CHCH_2C_3H_7 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \\ \\ Br\cdot + CH_3CH{=}CHC_3H_7 \underset{k_{-3}'}{\overset{k_3'}{\rightleftharpoons}} \end{array} \left[\begin{array}{c} CH_2{=}CH\dot{C}HC_3H_7 \\ \updownarrow \\ \cdot CH_2CH{=}CHC_3H_7 \end{array}\right] + HBr \qquad (3)$$

$$Br\cdot + CH_3CH{=}CHC_3H_7 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} CH_3CHBr\dot{C}HC_3H_7$$
$$(\text{or } CH_3\dot{C}HCHBrC_3H_7) \qquad (4)$$

$$\begin{array}{lcl} CH_3CHBr\dot{C}HC_3H_7 + HBr & \xrightarrow{k_5} & CH_3CHBrCH_2C_3H_7 + Br\cdot \\ (CH_3\dot{C}HCHBrC_3H_7) & & (CH_3CH_2CHBrC_3H_7) \end{array} \qquad (5)$$

Three termination steps are possible.

$$2Br\cdot \xrightarrow{k_6} Br_2 \qquad (6)$$

$$Br\cdot + C_6H_{12}Br\cdot \xrightarrow{k_7} C_6H_{12}Br_2 \qquad (7)$$

$$2C_6H_{12}Br\cdot \xrightarrow{k_8} \begin{array}{l} \text{dimerization or} \\ \text{disproportionation} \end{array} \qquad (8)$$

The predominant termination reaction will depend on the relative concentrations of Br· and $C_6H_{12}Br_2$.

The expression for the relative rates of formation of 1-bromohexane and 2-hexene can be readily derived.

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[5] P. I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964).

[6] P. I. Abell, *J. Am. Chem. Soc.*, **88**, 1346 (1966).

[7] (a) E. Jungerman and P. E. Spoerri, *J. Am. Oil Chemists' Soc.*, **35**, 393 (1958); (b) E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *J. Chem. Soc.*, 1937 (1948).

It is assumed that $k_{-3}' > k_{-3}$, which is reasonable on both steric and energetic grounds, *i.e.*, the primary allylic C–H bond is stronger than the secondary C–H bond. Making this assumption and the steady-state approximation, the expression for the ratio of 1-bromohexane and 2-hexene formed at low conversion is

$$\frac{(\text{1-bromohexane})}{(\text{2-hexene})} = \frac{k_1k_2(\text{HBr})}{k_3(k_{-1} + k_2(\text{HBr}))} \qquad (9)$$

At low HBr concentrations this expression simplifies to

$$\frac{(\text{1-bromohexane})}{(\text{2-hexene})} = \frac{k_1k_2(\text{HBr})}{k_3k_{-1}} \qquad (10)$$

Similar expressions in a slightly different form were derived by Adam, Gosselain, and Goldfinger[8] for the ratio of addition to allylic substitution by halogens. Since the temperature dependence of k_1 and k_2 should be smaller than k_{-1} and k_3, 1-bromohexane formation relative to 2-hexene should increase with decreasing temperature. This formation was observed. Also since 2-hexene is the principal precursor of 2- and 3-bromohexanes, the formation of 2- and 3-bromohexanes should decrease with decreasing temperature, which is consistent with observed phenomena.[9]

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[8] J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953).

[9] Recent experiments using ionizing radiation as the source of radical initiation (L. H. Gale, unpublished results) demonstrate that lowering the reaction temperature for addition of HBr to neat 1-hexene to − 13° yields a product with the composition: 97.0% 1-bromo-, 2.46% 2-bromo-, and 0.50% 3-bromohexane. The low yield of 3-bromohexane indicates that the double-bond migration is practically negligible at − 13° and that the bulk of the 2-bromohexane arises from ionic addition to 1-hexene. Also increasing the HBr concentration at 5° decreases the combined yield of 2-bromo- and 3-bromohexanes which is consistent with the behavior predicted by expression 10.

The Mass Spectrometry of Sulfonylureas. I. Mechanisms for the Loss of Sulfur Dioxide

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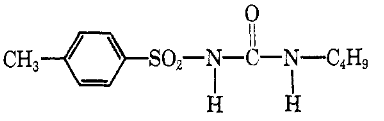
Abstract: The unique loss of 64 mass units (sulfur dioxide) observed in the mass spectrum of tolbutamide,[1] the most energetically favored fragmentation, has been shown by deuterium labeling and high-resolution mass spectrometry to involve two rearrangement mechanisms. The contribution of each was assessed individually from the accurate mass measurements of the pertinent fragment ions. Some thermal decomposition of the sample was observed due to a high source temperature and/or high inlet system temperature.

The mass spectrum of tolbutamide (I)[1] shows a loss of 64 mass units from the molecular ion which is attributed to the loss of SO_2. We became interested in the mechanism of this unique loss of the elements of SO_2 from the middle of this molecule. This paper reports studies to elucidate this mechanism.



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Skeletal rearrangements upon electron impact involving the loss of SO_2 had been reported previously, but no mechanisms were given to explain such losses.[2,3] Since the beginning of our studies similar losses of SO_2 have been reported for aliphatic sulfur compounds[4] and alkyl and aryl sulfonylhydrazones.[5]

Results and Discussion

The tolbutamide mass-spectral data are listed in Table I. The molecular ion was observed at m/e 270

Table I. Tolbutamide Mass Spectral Data

	% total ionization	
m/e	70 ev	19 ev
270	2.2	7.5
255	0.2	
241	0.3	
227	1.1	
215	0.4	
206	6.5	35.7
184	0.2	
171	0.6	0.5
163	0.3	
155	7.1	0.4
139	0.6	
115	2.0	1.5
108	14.0	19.4
107	5.3	11.5
99	3.2	3.3
91	15.4	0.1
73	3.2	3.1
72	2.3	0.5
65	4.6	
30	12.6	5.7

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[1] The Upjohn Co. trademark for tolbutamide is Orinase.

[2] S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964).

[3] J. ϕ. Madsen, C. Nolde, S.-O. Lawesson, G. Schroll, J. H. Bowie, and D. H. Williams, *Tetrahedron Letters*, No. **49**, 4377 (1965).

[4] A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.*, 358 (1966).

[5] R. G. Gillis and J. L. Occolowitz, *Tetrahedron Letters*, 1997 (1966).