The electrophilic addition of dimethylbromosulfonium bromide to conjugated enones: efficient synthesis of α-bromo enones

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Dimethylbromosulfonium bromide reacted readily with many enones at 0°C or lower to precipitate α-bromo-β-sulfonium conjugated enones. These salts eliminate a proton and dimethylsulfide readily with aqueous potassium carbonate to give excellent yields of α-bromo conjugated enones cleanly. The mechanism of the addition was explained by the bromonium ion initiated 1,4-addition followed by tautomerization of enol hypobromites.

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Le bromure de diméthylbromosulfonium réagit facilement avec plusieurs énones à 0°C ou à une température plus basse pour donner un précipité formé d'énones conjuguées α-bromo-β-sulfonium. Ces sels, en présence de carbonate de potassium en solution aqueuse, perdent facilement un proton et le diméthylsulfure en donnant des α-bromo énones conjuguées à l'état pur, avec un excellent rendement. On explique le mécanisme d'addition par l'ion bromonium qui initie une addition 1,4 suivie d'une tautomérisation des hypobromites d'énol.

[Traduit par le journal]

Dialkylbromosulfonium bromides are readily prepared from dialkylsulfides and bromine as relatively stable crystalline compounds (1–5) and their structures have been determined by X-ray analysis to have a S—Br bond (6). Dimethylbromosulfonium bromide is also formed from the interaction of dimethylsulfoxide with bromine or *N*-bromosuccinimide (7) in alcohols. This obviously involves an oxidation reaction by DMSO since it has been shown that HBr can catalyze the reduction of DMSO in the presence of H_2O to give dimethylsulfide and bromine.

In recent years, much interest has been directed toward dialkylhalosulfonium halides, in particular $(CH_3)_2SBr^+Br^-$ because of its ready availability, as synthetic reagents for various transformations. Pummerer type rearrangement is probably the earliest known reaction in which α-halosulfides are the product (1). The reaction type involving nucleophilic substitution at the α-carbon has been reported (1, 7).

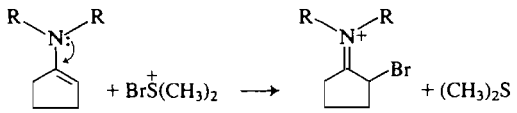
$$R-\overset{\overset{Br}{|}}{\underset{+}{S}}-CH_3 \quad X^- \rightarrow R-SBr + CH_3X$$

$$X = RO^-,\ OH^-,\ Br^-$$

However, nucleophilic attack at the cationic sulfur center is the more commonly observed reaction (3, 4, 8, 9). The reagent is also proposed as the donor of bromonium ion to electron-rich centers (5, 9). As shown by the reaction patterns, the reagents are versatile, but that also causes diversity of products. In some cases, control of the reaction conditions can promote a single reaction pathway enabling the reagents to be useful in synthetic chemistry.

$$Me_2\overset{+}{S}-Br + XH \rightarrow Me_2\overset{+}{S}-X + HBr$$

$$XH = R-OH\ (3);\ R_2NH\ (8),\ H_2C(CO_2R)_2\ (4),\ \text{epoxide}\ (9)$$



In pursuit of the application of dimethylbromosulfonium bromide in synthesis, we quite unexpectedly found that the reagent reacted efficiently and cleanly with certain α,β-unsaturated carbonyl compounds but not so efficiently with others. Our curiosity was further aroused by the fact that while the reagent was assumed to be an electrophile, it added efficiently to a so-called electron-poor conjugated double bond, in a manner very similar to electrophilic reactions. The addition reaction also led us to discover a simple way of preparing certain α-bromo-α,β-unsaturated carbonyl compounds in high yields and purity. This paper describes the chemistry pertaining to the synthetic processes and discusses the mechanism of the reactions.

Results

While the yellow solid bromodimethylsulfonium bromide, $(CH_3)_2S \cdot Br_2$ (**1**), could be prepared by mixing dimethyl sulfide and bromine in an inert solvent, it was more convenient to make it in acetonitrile and react it with α,β-unsaturated

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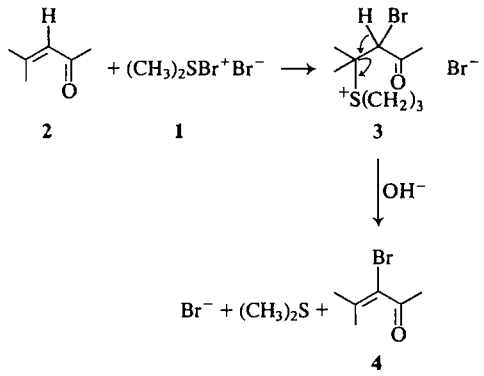
carbonyl compounds (**2**) *in situ* at temperatures lower than zero degrees. The rate of the reaction varied under these conditions depending on the degree of steric crowding and could be visually monitored by the changing of the yellow precipitate to a colorless solid which was identified as an α-bromo-β-dimethylsulfonium carbonyl compound (**3**). The sulfonium adducts **3** were stable enough at room temperature to be isolated and characterized by spectroscopic methods but not sufficiently stable for recrystallization. In aqueous solution the sulfonium adducts **3** underwent decomposition giving α-bromo enones **4** as the sole or the major product. However, simple dissolution of sulfonium adducts **3** in aqueous sodium bicarbonate solution resulted in a base catalyzed elimination of the α-proton and dimethylsulfide to provide, after extraction, excellent yields of practically pure α-bromo enones **4**.



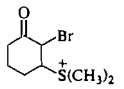
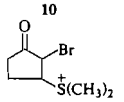
The overall reaction could be represented by the scheme shown above. The yields and spectroscopic parameters of the sulfonium adducts **3** and bromo enones **4** prepared by this process are summarized in Tables 1 and 2. Simplicity of operation, good yields of products, and the absence of by-products characterize this procedure as a superior method over the direct addition of bromine and base-catalyzed elimination to introduce the α-bromo group into certain α,β-unsaturated carbonyl compounds. The latter method (10–13) generally yields some by-products and requires distillation and recrystallization to obtain the reasonably pure products. In addition, several stereochemical features associated with the course and the products of the addition and elimination require some comments.

The reactions of $(CH_3)_2S \cdot Br_2$ with vinylmethyl ketone and acrolein were instantaneous even at −40°C, as judged by the disappearance of the yellow solid, whereas those with mesityl oxide and 2-cyclohexenenone were slow and only reasonably rapid in the vicinity of 0°C. The reaction with other enones 3-penten-2-one, crotonaldehyde, and 2-cyclopentenone was rapid at intermediate temperatures, e.g., at −10°C to ≈ −20°C. These observations clearly indicated the operation of steric crowding during the course of addition. The sulfonium adducts derived from acrolein and crotonaldehyde showed no (or superficial) carbonyl peaks but strong hydroxyl absorptions in the 3500 cm^{-1} region and were consistent with the *gem*-diol structure shown in **6** and **8**. This conclusion was supported by the lack of aldehydic signals in the 9–10 ppm region of the nmr spectra. However, in both cases, the sulfonium group was eliminated easily in the presence of bicarbonate, presumably occurring from the minor component of the aldehydic form in equilibrium with the hydrated form in solution. In aqueous solution, most of the sulfonium adducts **3** eliminated the sulfonium group slowly over a period of several days, except for **11** which, under nmr measurement conditions, did so rapidly to give 2-bromo-2-cyclopentenone **18**. While **9** is stable in storage, the copious amounts of **9** formed during the addition slowly decomposed when stirred at room temperature, by elimination of the sulfonium group, to give **16**, indicating steric acceleration. This may account for a lower yield of **18** (30–40%) when reaction was run at room temperature for a longer period.

The rates of $(CH_3)_2S \cdot Br_2$ addition to conjugated enones were significantly slower in less polar solvents. For example, the addition to acrolein in methylene chloride did not take place unless warmed to room temperature and took ten hours for the yellow color to disappear. It gave poorer yields of adduct **6**. In carbon tetrachloride the reaction was too slow at room temperature to be practical. The same trend was noted in the addition to mesityl oxide. In these cases, trimethylsulfonium bromide ($(CH_3)_3S^+Br$, singlet at 2.90 ppm) was formed in significant amounts.

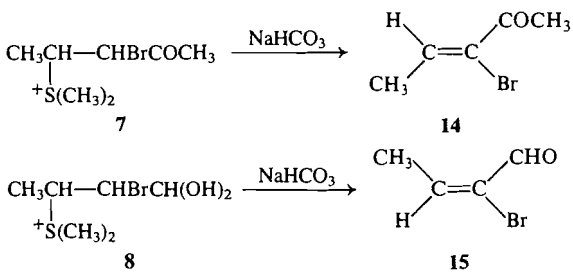
The addition of $(CH_3)_2S \cdot Br_2$ to some conjugated enones naturally led to the question of the stereochemistry of the resulting sulfonium adducts which were, in turn, related to the stereochemical course of the reaction. While the stereochemistry of sulfonium adduct **11** could not be determined due to its instability in solution, that of 2-bromo-3-sulfonium cyclohexanone **10** obviously had the *trans*-configuration (diequatorial) as shown by the nmr doublet at 4.38 ppm with $J = 10$ Hz. However, the presence of ≈5% of

TABLE 1. The addition of $(CH_3)_2SBr^+ \cdot Br^-$ to enones

Olefins	Adducts[a]	% Yields Melting point (°C)	Infrared (cm^{-1})[b]	Nuclear magnetic resonance (ppm)[c]
Vinylmethyl ketone	CH_2—$CHBrCOCH_3$ $^+S(CH_3)_2$ **5**	84 103–106 (dec.)	1720	5.24 (t, 1H, 6Hz), 4.02 (d, 2H, 6 Hz), 3.08 (s, 3H), 3.02 (s, 3H), 2.47 (s, 3H)
Acrolein	CH_2—$CHBrCHO$[d] $^+S(CH_3)_2$ **6**	88 70–75 (dec.)	3500	5.25 (d, 1H, 4 Hz), 4.45 (m, 1H), 3.96 (m, 2H), 3.06 (s, 3H), 3.02 (s, 3H)
3-Penten-2-one	CH_3CH—$CHBrCOCH_3$[f] $^+S(CH_3)_2$ **7**	92 58–61 (dec.)	1735	5.34 (d, 1H, 4 Hz), 4.25 (dq, 1H, 6.5 and 4 Hz), 3.02 (s, 3H), 3.00 (s, 3H), 2.52 (s, 3H), 1.59 (d, 3H, 7 Hz)
Crotonaldehyde	CH_3CH—$CHBrCH(OH)_2$[e] $^+S(CH_3)_2$ **8**	91 51–54 (dec.)	3500	5.27 (d, 1H, 5 Hz), 4.45 (m, 1H), 4.15 (m, 1H), 3.00 (s, 6H), 1.65 (d, 3H, 6.5 Hz)
Mesityloxide	$(CH_3)_2C$—$CHBrCOCH_3$ $^+S(CH_3)_2$ **9**	68 95–98 (dec.)	1715	5.15 (s, 1H), 2.92 (s, 3H), 2.90 (s, 3H), 2.50 (s, 3H), 1.74 (s, 6H)
2-Cyclohexenone	 **10**	96 45–47	1730	4.38 (d, 1H, 10 Hz), 4.03 (m, 1H), 2.97 (s, 3H), 2.86 (s, 3H), 1.6–2.4 (m, 6H)
2-Cyclopentenone	 **11**	96 51–52	1755	3.32 (s), 3.11 (s)[g]

[a] The adducts were isolated as sulfonium bromides and their ir and nmr spectra were given.
[b] The ir spectra were taken in Nujol or as KBr pellets.
[c] The nmr spectra were taken in D_2O using DSS as an internal standard.
[d] In CF_3CO_2H, it showed signals at 9.38 (broad s, 1H), 5.19 (t, 1H, 5 Hz), 4.10 (d, 2H, 5 Hz), 3.25 (s, 3H), 3.18 (s, 3H).
[e] The spectrum also showed weak signals at 5.30 (d, $J = 5$ Hz), 2.92 (s), 1.65 (s) for the minor isomer. In CF_3CO_2H it showed two sets of signals in a 1:1 ratio.
[f] On standing at the room temperature, there emerged another set of signals at 5.18 (d, 4 Hz), 4.10 (m), 3.02 (s), 2.88 (s), 2.52 (3), 1.64 (d, 7 Hz).
[g] On dissolution in D_2O, the compound eliminated $(CH_3)_2S$ spontaneously and showed weak signals of these two singlets corresponding to the dimethylsulfonium group.

another isomer was suggested by a small spike at 3.00 ppm (for a CH_3S^+-signal). Sulfonium adduct **8** showed a major and minor set of nmr signals in D_2O corresponding to the *erythro* and *threo* diastereoisomers. In trifluoroacetic acid, however, the two sets of signals were in the ratio of nearly 1:1. While 3-penten-2-one contained *trans* and *cis* isomers in a 10:1 ratio as shown by the nmr spectra, its sulfonium adduct **7** showed only one set of ^1H nmr signals in D_2O. This solution developed another set of signals, reaching a 1:1 ratio in two weeks. In trifluoroacetic acid solution, the change was much faster, reaching the equilibrium in four days. Assuming that the two sets of signals were derived from *erythro* and *threo* diastereoisomers, we must conclude isomerization occurred in solution. *It was noteworthy that the isomerization of 7 in D_2O solution was not accompanied by deuterium exchanges at the α- and β-position.*

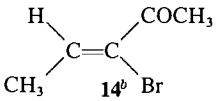
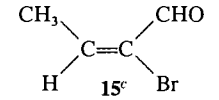


7 **14**

8 **15**

The base-promoted elimination of sulfonium adducts **7** and **8** also generates geometrical isomers of α-bromo enones **14** and **15**. The crude product obtained from base treatment of **8** showed a clear nmr spectrum in carbon tetrachloride for the single isomer **15**. The doublet at 2.14 ppm and the quartet at 7.18 ppm allowed us to assign the structure as shown. Another set of nmr signals developed gradually, reaching a 1:1 ratio after 3 days. This set

TABLE 2. Spectral data of α-bromo enones[a]

Compounds	Yield (%)	Infrared (cm^{-1})	^1H nuclear magnetic resonance (ppm)	^{13}C nuclear magnetic resonance (ppm)	Mass spectra (*m/e*, %)
CH_2=CBrCOCH$_3$ **12**	85	1710 1614	6.80 (d, 1H, 2 Hz), 6.32 (d, 1H, 2 Hz), 2.44 (s, 3H)	190.3 (s), 132.1 (s), 128.6 (t), 26.4 (q)	150(100), 148(99), 135(25), 133(27), 107(50), 105(52), 43(74)
CH_2=CBrCHO **13**	51[f]	1716 1603 2760	9.22 (s, 1H), 6.83, 6.77 (ABq, 1.9 Hz)	184.4 (d), 133.4 (s), 134.8 (t)	136(92), 135(17), 134(100), 133(14), 108(21), 106(17), 107(23), 105(25), 54(14)
 **14**[b]	84	1700 1615	7.18 (q, 1H, 6.8 Hz), 2.39 (s, 3H), 1.99 (d, 3H, 6.8 Hz)	190.0 (s), 129.1 (s), 139.2 (d), 27.0 (q), 18.5 (q)	164(93), 162(100), 149(93), 147(89), 121(42), 119(40), 43(69), 39(41)
 **15**[c]	86	1720 1630 2730	9.17 (s, 1H), 7.18 (q, 1H, 6.8 Hz), 2.14 (d, 3H, 6.8 Hz)	184.8 (d), 131.0 (s), 149.2 (d), 18.3 (q)	150(100), 148(95), 149(22), 147(20), 121(16), 119(18), 69(33), 41(25), 39(45)
$(CH_3)_2$C=CBrCOCH$_3$ **16**	94	1690	2.42 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H)	194.4 (s), 118.7 (s), 144.7 (s), 30.1 (q), 27.6 (q), 23.5 (q)	178(76), 176(73), 163(92), 161(100), 135(20), 133(22), 67(18), 53(46), 43(50)
 **17**[d]	92	1705 1605	7.26 (6, 1H, 4.5 Hz), 2.50 (m, 4H), 2.08 (m, 2H)	188.6 (s), 125.1 (s), 149.4 (d), 38.7 (t), 28.8 (t), 23.9 (t)	176(80), 174(80), 148(92), 146(100), 135(25), 133(28), 120(32), 118(36), 67(60), 55(26), 39(20)
 **18**[e]	93	1732 1597	7.27 (t, 1H, 3 Hz), 2.67 (m, 2H), 2.44(m, 2H)	199.1 (s), 127.4 (s), 160.3 (d), 32.4 (t), 28.4 (t)	162(100), 160(95), 134(38), 132(35), 81(23), 43(91)

[a]The ir and nmr spectra were recorded in CCl_4 solution; for the latter TMS was used as an internal standard. The molecular ion peaks gave the correct molecular weight by high resolution mass spectrometry.
[b]In CCl_4 solution, the ^1H nmr spectrum exhibited weak signals (10%) for the minor component at 6.42 (q, 6.8 Hz), 2.60 (s), 2.00 (d, 6.8 Hz); no isomerization occurred under the conditions (10).
[c]In CCl_4 solution, the ^1H nmr spectrum showed signals for the minor component at 9.40 (s), 7.50 (q, 7 Hz), 2.01 (d, 7 Hz); the ratio of the corresponding signals reached 1:1 in 3 days.
[d]Melting point 68–69°C (lit. (11) mp 69–71°C).
[e]Melting point 34–35°C (lit. (12) mp 39–39.5°C).
[f]The low yield arose from volatility of **13** (13).

showed a singlet at 9.40 ppm, a quartet at 7.50, and a doublet at 2.01 ppm, and was assigned to the structure with alternative geometry isomeric to **15**. On the contrary, the elimination of the sulfonium group from **7** gave **14** as the major product, with about 10% of the alternative isomer as shown by gc–ms and ^1H nmr. The latter was more volatile and easily removed by evaporation. Compound **14** was stable in CCl_4 solution.

The reagent $(CH_3)_2S \cdot Br_2$ reacted with cinnamaldehyde slowly at 0°C (but not at −30°C) and with ethyl cinnamate only at room temperature to give dibromo adducts without a trace of the sulfonium adducts. The reagent failed to add to isophorone and maleic anhydride and reacted sluggishly with 4-cholesten-3-one. In the presence of ethyl acrylate, the reagent reacted very slowly at 0°C and gave a complex mixture.

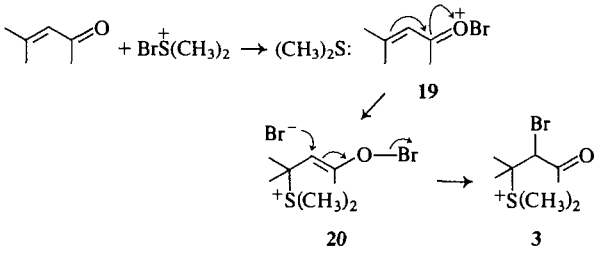
Discussion

The addition of $(CH_3)_2S \cdot Br_2$ to α,β-unsaturated carbonyl compounds is characterized by some unusual observations. Firstly, the addition occurs very rapidly even at −40°C in solid–solution mixture. Secondly, the rates of the addition are very sensitive to steric control, as seen by the failure to add to isophorone and 4-cholesten-3-one, and to electronic factors, as seen by the sluggish addition to conjugated esters. Thirdly, the reagent behaves as a bromine addition reagent with phenyl

conjugated α,β-unsaturated carbonyl compounds. Fourthly, the reagent completely fails to react with maleic anhydride which is brominated readily by Br_2 in carbon tetrachloride (14). Fifthly, the addition is dramatically retarded in less polar solvents such as methylene chloride. Finally, the addition is regiospecific, giving α-bromo-β-sulfonium carbonyl compounds, and stereoselective, giving predominantly one isomer where relevant. The evidence described above appears to indicate that the addition occurs by a mechanism of brominium ion initiated electrophilic addition to the conjugated double bond (15), or that of dimethylsulfide initiated nucleophilic attack at the β-carbon similar to the Michael type 1,4-addition. However, the attack of bromonium ion at the electron deficient olefinic bond of enones is not likely, nor is the manifested reactivity order in agreement with such an assumption. The latter idea suffers from the assumption that dimethylsulfide attacks at a disubstituted β-olefinic carbon in the mesityl oxide case; indeed, dimethylsulfide initiated addition is unknown as far as we are aware.

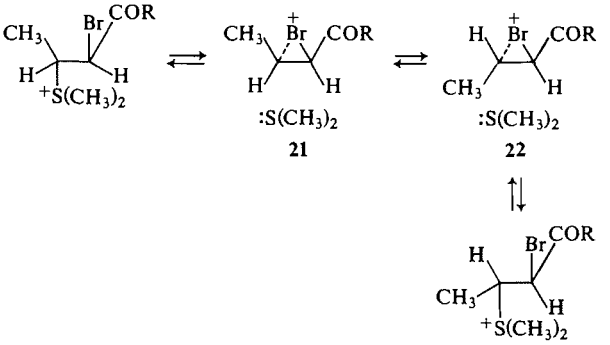
Alternatively, one may consider the sulfide cation radical (16) as the reactive species which initiates the addition by a chain process. Such a radical mechanism also suffers from inadequacy to explain dramatic solvent effects. Nor is it reasonable to use the sulfide cation radical to attack the β-carbon of a conjugated enone system. We have observed that the presence of air does not substantially alter the addition product pattern; this observation rules out the possibility of a radical mechanism.

The clue to the addition mechanism may rest on the reactivity order in which conjugated aldehydes react faster than conjugated ketones which, in turn, react faster than conjugated esters; that is, the more basic substrates react faster. It has been demonstrated that the addition of bromine to α,β-unsaturated ketones, aldehydes, and esters (and also other electron withdrawing groups) is catalyzed by acids involving the attack of the bromide (or an anionoid) at the β-carbon as the rate determining step (17). Reactivity is in the order of acrolein > crotonaldehyde >> cinnamaldehyde > ethyl cinnamate (18). We propose a similar mechanism as shown below to account for the addition. The reaction is initiated by the electrophilic attack of the brominium ion at the carbonyl oxygen to give the intermediate **19**. Such a mechanism can account for the observed regiospecificity and acceleration of the addition in polar solvent. In this mechanism the stereochemistry of the sulfonium adduct **3** is determined by tautomerization of the enol hypobromite **20** to **3** and may involve the attack of a bromide anion as a possible pathway. Therefore, irrespective of the *cis–trans* geometry of conjugated enones, the stereochemistry of the adducts **3** should be the same as determined by the tautomerization process as shown in the addition to 3-penten-2-one to give the single isomer **14**. It follows that the carbonyl group of conjugated esters is not as electron rich as that of conjugated enones to interact with $(CH)_2S—Br^+$ and therefore does not lead to a successful addition. Recently, the addition of bromine to conjugated enones has been reinvestigated in methylene chloride and from the reactivity pattern a similar mechanism has been proposed (19).



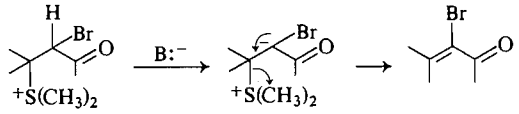
20 3

The observed isomerization of sulfonium adducts **7** and **8** from one diastereoisomer to the other in D_2O solution must involve the breaking and reformation of a bond at a chiral center. That this bond is not a C—H bond at the α and β chiral carbon centers is demonstrated by the lack of deuterium exchange in D_2O. A mechanism involving unsymmetrically bridged bromonium ions **21** and **22** may account for the isomerization. The isomerization of **7** occurs much faster in trifluoroacetic acid and, indeed, **8** also isomerizes in this solvent.



21 22

The base-promoted elimination of sulfonium adduct **3** is most likely to occur by an E1cb mechanism via the anion **23** and, thus, the stereochemistry of α-bromoenone **4** is determined by the stereoelectronic balance around the developing double bond. This mechanism can account for the elimination of diastereomeric



3 23 4

mixtures of **8** to give only one isomer **15** which rearranged slowly in carbon tetrachloride solution. In contrast, **14** is stable under similar conditions. Conjugated enones with the α-bromo group are versatile dienophiles in the Diels–Alder reaction, giving highly regiospecific adducts (20–24).

Experimental

Melting points were uncorrected. Reported nmr spectra were recorded on a Varian EM-360 or a Varian XL-100 and ir spectra with a Perkin–Elmer 457 spectrophotometer. Mass spectra were obtained with a Hewlett–Packard 5985 spectrometer. Gas chromatography was performed on a Varian 1400 instrument equipped with a SE-30 capillary column (45 ft × 0.28 mm). Reagent grade solvents were redistilled, and other chemicals were C.P. grade materials as supplied from commercial sources.

Preparation of dimethylbromosulfonium bromide

To a solution of dimethylsulfide (10 mL, 130 mmol) in methylene chloride (100 mL) cooled to −40°C under nitrogen, a bromine (15.01 g, 94 mmol) solution in methylene chloride (30 mL) was added in 30 min. A yellow precipitate formed immediately. The mixture was stirred for 10–20 min and ether (100 mL) was added. The precipitate was filtered, and washed with ether and pentane to afford bromodimethylsulfonium bromide (19.0 g, 91%).

Addition of dimethylbromosulfonium bromide to conjugated enones

Generally, the salt was formed *in situ* for the addition reaction. To a solution of dimethyl sulfide (1 to 2 mol equivalent) in acetonitrile (50–100 mL), cooled under nitrogen, a solution of bromine (≈ 20–100 mmol) in carbon tetrachloride (5 mL) was added, dropwise, at −40°C. The yellow precipitate was stirred at this temperature for 5 min and an enone (≈ 1–1.5 equivalent) was injected. Unhindered enones, such as vinylmethyl ketone or acrolein, reacted immediately at this temperature to give a colorless precipitate. Hindered carbonyl compounds, such as mesityloxide and 2-cyclohexenone, reacted at 0°C in 10–20 min to afford a colorless precipitate. To the mixture, ether (100 mL) was added. The precipitate was filtered and washed with ether and pentane and dried. The solid was generally stored in a freezing compartment.

Preparation of 2-bromo-α,β-unsaturated carbonyl compounds

A sulfonium salt (5–20 mmol) obtained from the above preparation was dissolved in 5% sodium bicarbonate solution (50–100 mL). The mixture was warmed for 10–15 min at room temperature and was extracted with methylene chloride. The methylene chloride solution was washed with water, dried, and evaporated to give the α-bromo enone. The product was pure enough to obtain the spectra shown in Table 2, but could be recrystallized or distilled. All α-bromo enones showed very intense molecular ion peaks which showed correct molecular weight by high resolution mass spectrometry.

Synthesis of α-bromoacrolein (an example)

Dimethylsulfide (5 mL) in acetonitrile (100 mL) was cooled at −40°C under nitrogen. Bromine (6 g) in carbon tetrachloride (5 mL) was added at −40°C to give the yellow precipitate. To this mixture acrolein (3 mL) was injected at −40°C, at which the yellow precipitate was changed to a white precipitate immediately. Ether (100 mL) was added to the mixture. The precipitate was filtered, washed, and dried on filter paper to give a white solid (8.0 g), mp 70–75°C(dec.). The solid was dissolved in water (50 mL) containing sodium bicarbonate (4.0 g). After warming up to 35°C for 15 min, the mixture was extracted with methylene chloride. The methylene chloride solution was worked up as usual and distilled over a short Vigreux column. The residue was distilled under a water pump vacuum to afford colorless α-bromoacrolein (1.85 g, 48% based on bromine); 45°C/25 Torr.

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