  Bull. Chem. Soc. Jpn., 53, 731—735 (1980)

Bromination of 9-Allyltriptycenes: Bromoolefin Formation and Lifetime of an Intervening Bromonium Ion

Shiro HATAKEYAMA, Tsutomu MITSUHASHI, and Michinori ŌKI*

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113

(Received July 7, 1979)

The bromination of 9-allyl-1,2,3,4-tetrachlorotriptycene affords a mixture of bromoolefins together with a minor quantity of the corresponding dibromide. By the examination of the reactions of model compounds, it is concluded that the first attack of bromine on the olefinic bond takes place in the *meso* rotamer and the resulted bromonium ion collapses either by attack of the tribromide ion to produce the dibromide or by internal rotation about the C_9–C_{allyl} bond followed by attack of the tribromide ion to produce the bromoolefin. Examination of the bromoolefin/dibromide ratios at various temperatures suggests that the activation energy for the attack of the tribromide ion on the bromonium ion is *ca.* 3 kcal/mol higher than the rotational barrier.

Since Roberts and Kimball postulated the intermediacy of a bridged ion in the bromination of alkenes,[1] there have been numerous studies on the behavior, of this ion[2] and its presence is now generally accepted. Curiously enough, however, no information about the lifetime of the bromonium ion has been available, although there has been a report that a bromonium ion formed during the bromination of a highly hindered alkene, adamantylideneadamantane, is stable.[3]

As a result of our work on restricted rotation,[4] we have been interested in reactivities of rotamers[5] and have extended the work to triptycene systems which show medium barriers to rotation. As has been briefly reported,[6] the bromination of 9-allyl-1,2,3,4-tetrachlorotriptycene (**2**) was found to afford substitution products together with a normal adduct. This is a striking fact since substitution is known to occur during the bromination if the olefin is conjugated[7] but no instance is reported for such substitution, to the best of our knowledge, in the case of unconjugated olefins. Thus the finding prompted us to investigate the driving force for the substitution reaction by carrying out similar reactions with related compounds.

We wish to furnish evidence in this paper for that the bromoolefin is produced because an intermediate bromonium ion formed from the *meso* rotamer of the compound in question undergoes internal rotation and the *dl*-rotamers subsequently formed are stabilized by the participation of the neighboring chloro group. As a by-product of the investigation, rough estimation of the lifetime of the bromonium ion becomes possible. The process of the estimation will be discussed in detail.

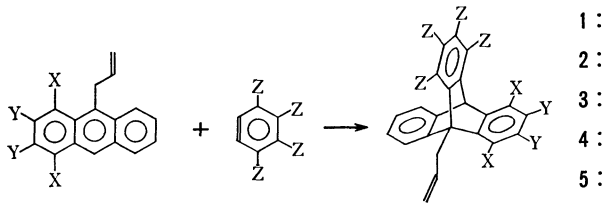
Experimental

Materials. 9-Allyltriptycenes were prepared by the Diels-Alder reactions of 9-allylanthracenes with benzynes, as illustrated in the scheme below. 9-Allylanthracenes were obtained, according to the procedure presented by Mosnaim *et al.*,[8] by the Grignard reaction of allylmagnesium chloride with substituted anthrone, followed by dehydration of the products. The purity of allylanthracenes was checked by ^{1}H NMR spectra and they were directly used for subsequent reactions.

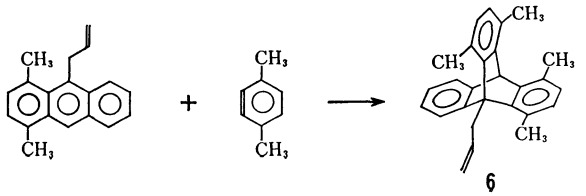
9-Allyl-1,4-dimethylanthracene. 1,4-Dimethylanthrone[9] (5 g, 0.02 mol) was added in small portions to a stirred solution of allylmagnesium chloride (0.07 mol) in ether. After the addition was completed, 50 ml of dry tetrahydrofuran was added and the mixture was refluxed for another hour. The mixture was cooled and the Grignard complex was decomposed with dilute hydrochloric acid. Organic layer was separated, treated with concentrated hydrochloric acid for dehydration of the product, and washed with water. The dried solution was evaporated and the residue was chromatographed on silica gel, using hexane as an eluent. ^{1}H NMR ($CDCl_3$, δ): 2.76 (3H, s), 2.99 (3H, s), 4.3—5.4 (4H, m), 6.0—6.8 (1H, m), 7.15 (2H, s), 7.3—8.3 (4H, m), 8.49 (1H, s).

9-Allyl-2,3-dichloroanthracene was prepared similarly by using 2,3-dichloroanthrone.[10] ^{1}H NMR ($CDCl_3$, δ): 3.9—4.2 (2H, m), 4.5—5.2 (2H, m), 5.7—6.4 (1H, m), 7.1—8.2 (7H, m).

9-Allyl-1,2,3,4-tetrachloroanthracene was also prepared by using 1,2,3,4-tetrachloroanthrone.[11] In this case, phosphorus pentaoxide was used for dehydration in place of concentrated hydrochloric acid. ^{1}H NMR ($CDCl_3$, δ): 4.3—4.5 (2H, m), 4.7—5.4 (2H, m), 6.0—6.6 (1H, m), 7.3—8.3 (4H,



1 : X=Y=Z=H
2 : X=Y=H, Z=Cl
3 : X=CH_3, Y=Z=H
4 : X=Z=H, Y=Cl
5 : X=Y=Z=Cl



6

m), 8.60 (1H, s).

9-Allyltriptycene (1). To a refluxing solution of 3.5 g (0.03 mol) of isopentyl nitrite and 4.4 g (0.02 mol) of 9-allylanthracene in 30 ml of dichloromethane was added 4.1 g (0.03 mol) of anthranilic acid in 20 ml of acetone over a period of 2 h. The reaction mixture was heated for 1 h and cooled. The solvent was evaporated *in vacuo* and the residue was taken up in benzene. Chromatography on alumina, using hexane as an eluent, gave 4 g (68% yield) of **1**. The compound was recrystallized from hexane, mp 148—148.5 °C. Found: C, 93.65; H, 5.88%. Calcd for $C_{23}H_{18}$: C, 93.82; H, 6.18%. ^{1}H NMR ($CDCl_3$, δ): 3.6—3.9 (2H, m), 5.2—5.8 (2H, m), 5.36 (1H, s), 6.0—6.8 (1H, m), 6.8—7.6 (12H, m).

9-Allyl-1,4-dimethyltriptycene (3), mp 134—134.5 °C, was similarly prepared by using 9-allyl-1,4-dimethylanthracene. The yield was 65%. Found: C, 93.21; H, 6.60%. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88%. ^{1}H NMR ($CDCl_3$, δ): 2.39 (3H, s), 2.54 (3H, s), 4.0—4.3 (2H, m), 5.0—5.7 (2H, m), 5.58 (1H, s), 5.8—6.7 (1H, m), 6.65 (2H, q, J_{AB}= 8.0 Hz, $\Delta\delta_{AB}$=4.1 Hz), 6.8—7.6 (8H, m).

9-Allyl-2,3-dichlorotriptycene (4), mp 234.5—235 °C, was similarly prepared in 65% yield and was recrystallized from dichloromethane–hexane. Found: C, 75.74; H, 4.30; Cl, 19.99%. Calcd for $C_{23}H_{16}Cl_2$: C, 76.04; H, 4.44; Cl, 19.52%. ^{1}H NMR ($CDCl_3$, δ): 3.6—3.9 (2H, m), 5.30 (1H, s), 5.2—5.8 (2H, m), 6.0—6.7 (1H, m), 6.9—7.6 (10H, m).

9-Allyl-1,2,3,4-tetrachlorotriptycene (2) was obtained by the reaction of 9-allylanthracene with tetrachlorobenzyne which was generated by the action of isopentyl nitrite on tetrachloroanthranilic acid.[12] The yield was 15%. It was recrystallized from chloroform–ether–hexane, mp 257.5—258 °C. Found: C, 64.17; H, 3.10; Cl, 32.61%. Calcd for $C_{23}H_{14}Cl_4$: C, 63.92; H, 3.27; Cl, 32.81%. ^{1}H NMR ($CDCl_3$, δ): 4.2—4.6 (2H, m), 5.1—5.7 (2H, m), 5.8—6.3 (1H, m), 6.02 (1H, s), 6.9—7.7 (8H, m). ^{13}C NMR ($CDCl_3$, ppm from TMS): 34.1, 52.6, 56.5, 59.8, 115.8, 123.0, 123.8, 123.9, 124.0, 124.4, 124.8, 126.7, 129.7, 135.7, 142.6, 142.8, 145.5.

9-Allyl-1,4,5,8-tetramethyltriptycene (6), mp 187.5—188.5 °C was prepared from 9-allyl-1,4-dimethylanthracene, isopentyl nitrite, and 3,6-dimethylanthranilic acid[13] in 60% yield. Found: C, 92.68; H, 7.56%. Calcd for $C_{27}H_{26}$: C, 92.52; H, 7.48%. ^{1}H NMR ($CDCl_3$, δ): 2.41 (3H, s), 2.50 (3H, s), 2.62 (6H, s), 4.0—4.7 (2H, m), 5.0—5.7 (2H, m), 5.7—6.3 (1H, m), 5.88 (1H, s), 6.5—7.7 (8H, m).

9-Allyl-1,2,3,4,5,6,7,8-octachlorotriptycene (5), mp 256.5—257.5 °C, was prepared from 9-allyl-1,2,3,4-tetrachloroanthracene, isopentyl nitrite, and tetrachloroanthranilic acid in 10% yield. It was recrystallized from dichloromethane–hexane and its purity was checked by the ^{1}H NMR spectrum. Mass spectrum showed widely distributed molecular ion peaks at 566, 568, 570, 572, 574, and 576 in accord with the natural abundance of ^{35}Cl and ^{37}Cl. The most intensive peak was 570. ^{1}H NMR ($CDCl_3$, δ): 4.0—4.3 (1H, m), 5.0—5.9 (4H, m), 6.70 (1H, s), 7.0—7.9 (4H, m).

Bromination. 9-Allyltriptycenes were brominated with a large excess of bromine in chloroform with stirring overnight. To the reaction mixture, an excess of pentenes was added and the solvent was evaporated *in vacuo*. In the cases of dimethyl and tetramethyl derivatives, the brominations were carried out by using equimolar amounts of bromine with stirring for 3 d since the substitution at the benzene nuclei occurred in the presence of excessive bromine. The ^{1}H NMR spectra of the resulting residue showed that the bromination was almost complete under the reaction conditions. A typical example follows.

To a solution of 0.15 g (0.94 mmol) of bromine in 20 ml of chloroform was added 10 ml of a chloroform solution containing 42.0 mg (0.095 mmol) of **2** and the mixture was stirred overnight at 0 °C. After treated with pentenes, the mixture was evaporated. The residue was chromatographed on alumina with hexane as an eluent. The first fraction contained *trans*- and *cis*-bromoolefins (**10**), and the second afforded dibromide (**9**). Careful chromatography and repeated recrystallization of the bromoolefin mixture from dichloromethane–hexane gave *trans*-**10** as a pure specimen.

trans-**10**, mp 239—239.5 °C. Found: C, 53.90; H, 2.38; Br, 15.50; Cl, 27.51%. Calcd for $C_{23}H_{13}BrCl_4$: C, 54.05; H, 2.57; Br, 15.63; Cl, 27.75%. ^{1}H NMR ($CDCl_3$, δ); 4.2—4.5 (2H, m), 6.04 (1H, s), 6.1—6.8 (2H, m), 6.9—7.7 (8H, m).

The following ^{1}H NMR data for the *cis* isomer were obtained by subtracting the signals due to the *trans* isomer from those of the *cis-trans* mixture: 4.2—4.5 (2H, m), 6.03 (1H, s), 6.4—6.6 (2H, m), 7.0—7.6 (8H, m).

9, mp 195—196.5 °C (from dichloromethane–hexane). Found: C, 46.69; H, 2.27; Br, 27.42; Cl, 24.33%. Calcd for $C_{23}H_{14}Br_2Cl_4$: C, 46.67; H, 2.38; Br, 27.00; Cl, 23.95%. ^{1}H NMR ($CDCl_3$, δ): 3.6—4.2 (2H, m), 4.2—4.6 (2H, m), 4.7—5.2 (1H, m), 6.01 (1H, s), 6.9—8.0 (8H, m).

Bromination of **1** gave 9-(2,3-dibromopropyl)triptycene only. It was recrystallized from chloroform–hexane, mp 201—202 °C. Found: C, 60.89; H, 3.82; Br, 35.48%. Calcd for $C_{23}H_{18}Br_2$: C, 60.82; H, 4.00; Br, 35.18%. ^{1}H NMR ($CDCl_3$, δ): 3.84 (2H, d, J=6.5 Hz), 4.0—4.6 (2H, m), 5.0—5.4 (1H, m), 5.32 (1H, s), 6.8—7.6 (12H, m).

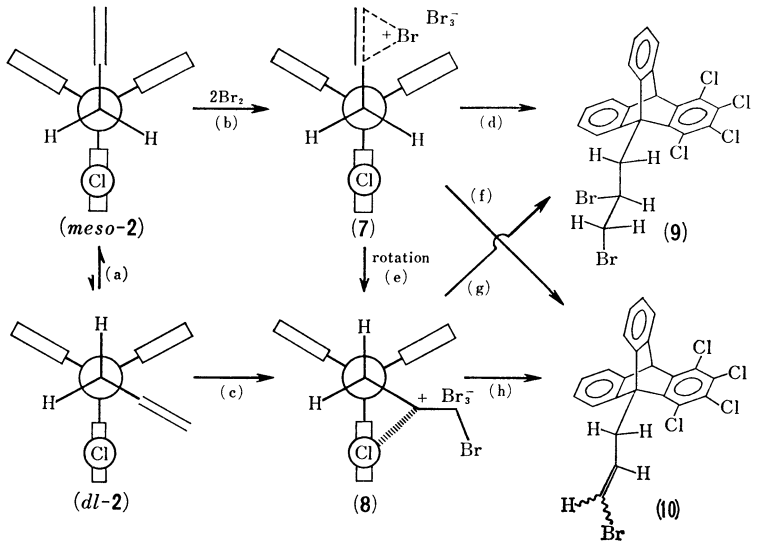
Bromination of **5** gave a product which did not show any NMR signals ascribable to the corresponding dibromide but those consistent with the structure of bromoolefins. The mixture of bromoolefins resisted to separation. Mass spectrum showed widely distributed molecular ion peaks at 644, 646, 648, 650, 652, 654, 656, and 658 in accord with the olefinic structure and the natural abundance of ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br. The most intensive peak was 648. ^{1}H NMR ($CDCl_3$, δ): 3.7—4.3 (1H, m), 4.9—5.5 (1H, m), 6.0—6.7 (2H, m), 6.69 (1H, s), 7.0—7.8 (4H, m).

Bromination of **4** gave 9-(2,3-dibromopropyl)-2,3-dichlorotriptycene only. It was recrystallized from dichloromethane–hexane, mp 103—104 °C. Found: C, 52.97; H, 3.18; Br, 31.01; Cl, 13.76%. Calcd for $C_{23}H_{16}Br_2Cl_2$: C, 52.81; H, 3.08; Br, 30.55; Cl, 13.56%. ^{1}H NMR ($CDCl_3$, δ): 3.7—4.3 (4H, m), 5.0—5.4 (1H, m), 5.27 (1H, s), 6.9—7.6 (10H, m).

Bromination of **3** afforded 9-(2,3-dibromopropyl)-1,4-dimethyltriptycene only. It was recrystallized from dichloromethane–hexane, mp 199—200 °C. Found: C, 62.23; H, 4.37; Br, 33.51%. Calcd for $C_{25}H_{22}Br_2$: C, 62.26; H, 4.60; Br, 33.14%. ^{1}H NMR ($CDCl_3$, δ): 2.33 (3H, s), 2.49 (3H, s), 3.5—4.3 (4H, m), 4.8—5.2 (1H, m), 5.55 (1H, s), 6.47 (2H, s), 6.8—7.9 (8H, m).

Kinetics. Competitive reactions were carried out as follows. An equimolar mixture of **1** and one of other 9-allyltriptycenes was added to a solution of an equimolar amount of bromine in chloroform which was pre-cooled to 0 °C. The mixture was stirred for 3 d at 0 °C. Relative reaction rate was calculated by measuring the amount of unreacted starting materials with a Waters M-6000 high pressure liquid chromatography apparatus, using hexachlorobenzene as the internal standard. The following equation was used to obtain relative rates.

$$k_N/k_1 = \log\frac{[N]}{[N]_0} \Big/ \log\frac{[\mathbf{1}]}{[\mathbf{1}]_0}$$



where N denotes the compound in question and subscript 0 the initial state.

The following is a typical procedure. A solution of 15.5 mg (5.3×10^{-5} mol) of **1**, 22.9 mg (5.3×10^{-5} mol) of **2**, 8.4 mg (5.3×10^{-5} mol) of bromine, and 10.7 mg of C_6Cl_6 in 7 ml of chloroform was stirred for 3 d at 0 °C. Then an excessive amount of pentenes was added and the solution was submitted for analysis. The relative rate of **2** to **1** was 0.47.

Temperature Dependence of the Product Ratio in the Bromination of 2. Bromination of **2** (8 mg of **2** and 27 mg of bromine in 6 ml of chloroform) was carried out at 40 °C, 20 °C, 0 °C, and −17 °C. After 1 h the unreacted bromine was removed by pentenes. Under these conditions, a considerable amount of **2** was recovered. The product ratio was determined by means of high pressure liquid chromatography.

Spectral Measurement. ^{1}H NMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. ^{13}C NMR spectra were obtained on a JEOL FX-60 spectrometer operating at 15.4 MHz.

Discussion

9-Allyl-1,2,3,4-tetrachlorotriptycene gave a mixture of *cis-trans* bromoolefins as a major product along with a normal adduct. This is anomalous in that the bromination of normal unconjugated olefins gives addition products and it is conjugated olefins that gives substitution products. The bromoolefin might be considered to be not a primary product: it may be formed as a result of dehydrobromination of a primary product, which is the normal product. Therefore, the dibromide was treated under the reaction conditions. No bromoolefin was found, however. Thus the bromoolefin must be a primaty product.

Possible pathways leading to the dibromide and the bromoolefin are shown in the above scheme. Advantages and disadvantages of these paths will be discussed by the experimental and available data.

As to the conformations of the molecule, the triptycene skeleton is rigid and thus there are two axes about which conformational changes are possible: C_9–C_{allyl} and C_{CH_2}–C_{vinyl} bonds. Although it is generally recognized that the most stable conformation of propene is that in which the C=C bond and one of the C–H's in the methyl eclipse with each other,[14] that kind of conformation is not stable in the present case because of the repulsion between the vinyl moiety and the peri-substituents. Rather it may be reasonable to assume that, as was the case in 9-benzyltriptycenes,[15] the vinyl group takes a conformation in which the π-system bisects the H–C–H angle of the allyl-methylene group. There are still two possible conformations after assuming the relation between the methylene and the vinyl groups: a =CH inside conformation and a C=C inside conformation. We are convinced that the C=C inside conformation is much less stable due to the steric effects.[16]

Since both the ^{1}H NMR spectra of 9-allyl-1,2,3,4-tetrachlorotriptycene (**2**) at ambient and low temperatures did not show any of the AB type signal but a rather sharp signal for the CH_2 group in the allyl, the compound may be assumed to exist as the *meso* form exclusively. The ^{13}C NMR spectrum of **2** supported the assumption: at −34 °C, where the internal rotation should be frozen,[17] the ^{13}C NMR spectrum gave lines in accordance with the molecular structure of C_{2v} symmetry. Thus the equilibrium shown as (a) in the scheme is lopsided in favor of the *meso* form.

However, these observations may not be taken as direct evidence for that the reaction takes place from the *meso* form, since the *dl* form, being more reactive due to the chloro participation, might react exclusively albeit their trace population. Therefore, another support is, at least, needed to exclude the reaction in the *dl*-conformation (path c).

We took advantage of reactions of model compounds to diagnose the presence or the absence of the reaction paths. As described in the Experimental section, brominations of 9-allyltriptycene (**1**) and its 2,3-dichloro (**4**) and 1,4-dimethyl (**3**) derivatives afforded only the corresponding addition products: formation of the substituted products is limited to the system carrying a peri-chloro group. The results indicate that the bromoolefin formation is not a result of the steric hindrance of the peri-substituent, since, if it were the case, the 1,4-dimethyl derivative should have given a bromoolefin. Neither the bromoolefin forma-

TABLE 1. RELATIVE BROMINATION RATES OF SUBSTITUTED 9-ALLYLTRIPTYCENES

Substrate	Substituent	Relative rate
1	none	1.00
2	1,2,3,4-Cl_4	0.47
3	1,4-$(CH_3)_2$	0.74
4	2,3-Cl_2	0.76
5	1,2,3,4,5,6,7,8-Cl_8	≈ 0
6	1,4,5,8-$(CH_3)_4$	<0.09

tion is attributed to the inductive effect, because the 2,3-dichloro derivative failed to give any of the corresponding bromoolefin. The formation of the bromoolefin from the *meso* bromonium ion (**7**) may thus be unlikely (path f). A logical intermediate will then be a chloronium ion (**8**) or a carbocation stabilized by a neighboring chloro group.

Neighboring chloro participation is present if the group is in the vicinity of a cationic center[18] and 5-membered cyclic chloronium ion have been postulated.[19] Since the cationic center and the chloro group are to form a 6-membered ring, this kind of stabilization is expected. Then a problem arises: is the stabilized cation directly formed from the *dl* form (path c) or is it formed by the attack of bromine on the *meso* form followed by the internal rotation (paths b and e)?

9-Allyl-1,2,3,4,5,6,7,8-octachlorotriptycene (**5**) was used as a model compound for the diagnosis. ^1H NMR spectra of this compound showed an AB pattern split by the adjacent protons but no signal ascribable to CH_2 protons of the *meso* form was observed. This is reasonable because the *meso* form, having the vinyl group inbetween the two tetrachlorobenzo bridges, is unstable relative to the *dl* form in this compound. The action of a large excess of bromine on **5** in chloroform at room temperature afforded the corresponding substituted product only in an almost quantitative yield after standing overnight. This observation suggests that the *dl* form of **2**, if reacted at all, affords only the substitution products and could in principle mean that the reaction occurs from the *dl* form of **5**.

We then ran competitive reactions to obtain further information about the reaction rates. The results are shown in Table 1. The relative rates, taken that of unsubstituted 9-allyl-triptycene (**1**) as a standard, suggest that substitution by chloro groups remote from the reaction site retards the reaction to a small extent (compare **1** and **4**). Therefore, the less reactivity of compound **2**, compared to **3**, must be derived by the electronic effect, because the steric effects in these compounds are almost the same. Another example of this sort is found in the defference in reactivities of **5** and **6**: **5** showed almost zero reactivity in the presence of **1**, whereas **6** reacted definitely, although a little, in spite of their similar steric environments. The low reactivities of **5** and **6** may now be taken as evidence for that the bromination of **2** does not take place in the *dl* form but in the *meso* form exclusively. Thus we rule out the path c: the bromination of **2** must proceed *via* path b.

As to the formation of two kinds of products, the dibromide and the bromoolefin, two pathways are still possible, although the intervention of the *dl* form of **2** is now excluded. A bridged bromonium ion (**7**) formed by the attack of bromine on the olefin in the *meso* form may react with the tribromide anion to afford the adduct (path d). Alternatively, **7** may undergo internal rotation to form the *dl* form which may quickly change to the chloronium ion (**8**) (path e). The chloronium ion may be attacked by the tribromide ion at the inside carbon to form the dibromide (path g) or at the proton of the outside carbon to form the bromoolefin (path h). The formation of the dibromide from the chloronium ion (path g), however, may be rejected for the following reasons. The octachloro compound (**5**) failed to give any of the corresponding dibromide. Since a bromonium ion formed from **5** may collapse to a chloronium ion easily, a dibromide should have been found in the bromination products, if the chloronium ion were to produce the dibromide. This is reasonable because the inside carbon in the chloronium ion (**8**) is sterically protected and more exposed protons of the bromomethyl group will be vulnerable to the attack.

Although it is not possible to rigorously exclude the possibility that the once-formed chloronium ion undergoes internal rotation to revert to the *meso* bromonium ion (**7**), we believe this will not occur because of the stability of the chloronium ion. The chloronium ion will be attacked to give the bromoolefins before the internal rotation.

Having established the paths of the reaction, we come to an interesting problem. It is most likely that both the internal rotation and the attack of the bromonium ion by the tribromide occur from the bromonium-tribromide ion pair.[20] The reasons are three fold: bromide salts are not added which would enhance the attack by the bromide ion, the bulkiness of the triptycyl group efficiently hinders the solvation of the charge center of the bromonium ion to disfavor the formation of free ions, and the low polarity of the solvent should be unfavorable for the formation of free ions. We may then approximate that both the internal rotation and the formation of the dibromide are unimolecular competitive reactions occurring from the same ion pair, although it can be argued, strictly saying, that the ion pair may have to dissociate for the rotation, the collapse of the solvent-separated ion pair is not purely unimolecular, *etc.* Then examination of the temperature dependence of the product ratio (**10**/**9**) will produce the ratio of rate constants and the difference in kinetic parameters of the two processes.

The results of the temperature dependence study of the ratios **10**/**9** are shown in Table 2. The ratio increases with the decreasing temperature. The Arrhenius polt of the data yields the difference in the activation energies as 3.0 kcal/mol and that in the entropies of activation as 8.0 e.u. The absolute value of the activation energy for rotation can not be obtained at the present time, but we tentatively assume that the size of the ion pair is roughly the same with that of a phenly group. Then the barrier to rotation

Table 2. Formation ratios of the bromoolefins *vs.* the adduct in the bromination of compound **2** at various temperatures

Temp/°C	Ratio (substitution/addition)
40.7	1.54
20.0	2.40
0.0	3.09
−17.0	7.36

(E_a 13.1 kcal/mol, ΔS^* −6.0 e.u.) is known for a model compound, 9-benzyl-1,2,3,4-tetrachlorotriptycene.[21] This indicates that the collapse of the ion pair requires thermal energy corresponding to these kinetic parameters: the energy of activation for rotation will be about 13 kcal/mol and that for the reaction of the ion pair about 16 kcal/mol. Using these values, we estimate the half life of the bridged bromonium ion as 0.1 s at 0 °C. This is by no means the general half life of bromonium ions but, we feel, is a special case where the lifetime of the intermediate is exceptionally long due to the steric conditions.

The change in entropies of activation, as observed from the ratio (**10**/**9**) is nearly equal to that for the rotation of 9-benzyl-1,2,3,4-tetrachlorotriptycene. If we rely upon the entropy of activation obtained by the DNMR method,[22] it follows that the activation entropy for the reaction of the bromonium ion with the tribromide ion is close to zero. This value seems to be plausible since the collapse of an ion pair is a unimolecular reaction and concurrent occurence of the bond formation (C–Br) and the bond cleavage (Br–Br_2) will compensate to result in a small entropy change.

The lack of the reactivity of the bromoolefins toward an excess of bromine is not limited under the conditions mentioned above. The isolated bromoolefins are also inert to bromine. Although the reason for this inertness is not well understood at the present time, we believe the steric effects must be playing an important role.

References

1) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).
2) J. G. Traynham, *J. Chem. Educ.*, **40**, 392 (1963).
3) J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Commun.*, **1969**, 907.
4) M. Ōki, *Angew. Chem. Int. Ed. Engl.*, **15**, 87 (1976).
5) M. Nakamura, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **50**, 1097 (1977).
6) S. Hatakeyama, T. Mitsuhashi, and M. Ōki, *Chem. Lett.*, **1978**, 559.
7) K. E. Koenig and Wm. P. Weber, *Tetrahedron Lett.*, **1973**, 2533.
8) D. Mosnaim, D. C. Nonhebel, and J. A. Russel, *Tetrahedron*, **25**, 3485 (1969).
9) F. Bell and D. H. Waring, *J. Chem. Soc.*, **1949**, 267.
10) E. de Barnett, M. A. Mathews, and J. L. Wiltshire, *Rec. Trav. Chim.*, **45**, 558 (1926).
11) P. Kniel, *Helv. Chim. Acta*, **46**, 492 (1963).
12) V. Villiger and L. Blangey, *Ber.*, **42**, 3549 (1909).
13) F. Mayer, W. Schäfer, and J. Rosenbach, *Arch Pharm.*, **267**, 571 (1929): S. Gronowitz and G. Hansen, *Ark. Kemi.*, **27**, 145 (1967).
14) D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958).
15) F. Suzuki and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 596 (1975).
16) X-Ray data of 9-acetonyl-1,2,3,4-tetrachlorotriptycene suggest that the acetyl group assumes not a methyl-inside but an O-inside conformation. This is rationalized by the steric effects, a smaller group taking the inside position. N. Nogami, Ph. D. Thesis, The University of Tokyo, 1978.
17) We have numerous examples that show frozen rotation on the NMR time scale. The coalescence temperatures of the triptycenes which carry XCH_2-type substituent in the 9-position are generally around −10 °C. See also H. Nakanishi and O. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 1777 (1978).
18) P. E. Peterson and J. F. Coffey, *J. Am. Chem. Soc.*, **93**, 5208 (1971).
19) P. E. Peterson and E. V. P. Tao, *J. Am. Chem. Soc.*, **86**, 4503 (1964); G. A. Olah and P. E. Peterson, *J. Am. Chem. Soc.*, **90**, 4675 (1968).
20) R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967); R. J. Abraham and J. R. Monasterios, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 1446.
21) M. Ōki, M. Kono, H. Kihara, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **52**, 1686 (1979).
22) Although entropies of activation obtained by the DNMR method must be treated carefully (R. R. Shoup, E. D. Becker, and M. L. McNiel, *J. Phys. Chem.*, **76**, 71 (1972)), it is also true that carefully derived ΔS^*'s are reliable at least in some instances (M. Nakamura, H. Kihara, N. Nakamura, and M. Ōki, *Org. Magn. Reson.*, **12**, 702 (1979)).