Bromine Addition Reaction to Olefins with Magnesium Bromide and Aroyl Peroxides

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(Received June 11, 1973)

When $MgBr_2$ prepared in anhydrous tetrahydrofuran was added to a mixture of olefin and benzoyl peroxide, the peroxide decomposed at a moderate rate at room temperature. Olefin dibromide and magnesium benzoate were obtained in nearly quantitative yields. The effects of *p*- and *m*-substituents of peroxide and of the structure of olefin were studied. A complex consisting of $MgBr_2$ and peroxide was formed. Abstraction of brominium cation from the complex by the olefinic double bond was proposed.

The addition of bromine to cyclohexene in an orange-colored solution of a complex prepared from PhCOOMgBr and benzoyl peroxide(BPO) in tetrahydrofuran(THF) has been reported.[1] The results and the fact that $MgBr_2$ is considered to be a component of Grignard reagents[2] prompted us to examine the reaction of BPO and $MgBr_2$ in anhydrous THF. When equimolar BPO was added to a solution of $MgBr_2$, an orange color appeared. The colored solution has the ability to add bromine to cyclohexene giving *trans*-1,2-dibromocyclohexane in a good yield. Results of studies of this reaction are given in this paper.

Results and Discussion

The same reaction was reported by Yang and Lawesson,[3] who obtained *trans*-1,2-dibromocyclohexane almost quantitatively. They suggested the reaction to be a simple addition of molecular bromine produced in the reaction of BPO and $MgBr_2$ (Reaction 1), but gave no precise mechanism. Whereas they used ethyl ether

$$(PhCOO)_2 + MgBr_2 \rightarrow (PhCOO)_2Mg + Br_2 \qquad (1)$$

as solvent, we used THF. It should be noted that ethyl ether cannot maintain the reaction components in solution and forms a heavy precipitate easily. In contrast, the reaction mixture is homogeneous in THF when the concentration is about 40 mmol/l.

When equimolar BPO was added to a clear solution of $MgBr_2$ in anhydrous THF[4] at 15 °C, the mixture turned yellow, deepening to orange in the course of 45 to 60 min. No more deepening took place after the solution has been left to stand for several hours under nitrogen atmosphere. The color is similar to that of "Complex II"[5] prepared from PhCOOMgBr and a half equimolar BPO. The coloration is not due to molecular bromine, since Br_2 attacks the THF molecule easily even at 0 °C giving hydrogen bromide. Neither molecular bromine nor hydrogen bromide was detected in the distillate of the orange colored solution. The color did not fade and the peroxide-content(determined by iodometry) did not decrease when the solution was left to stand overnight. Turbidity appeared when ethyl ether was added to the concentrated solution at 0 °C. Orange-red crystals were obtained after the mixture was left to stand in a refrigerator for about two weeks. Thus, it was confirmed that $MgBr_2$ and BPO from a complex(Reaction 2), hereafter called Complex III.[5] Reaction

$$(PhCOO)_2 + MgBr_2 \rightleftarrows [\text{Complex III}] \qquad (2)$$

2 will be expressed as an equilibrium process.

When equimolar cyclohexene was added to the solution of Complex III, the peroxide-content decreased and became nearly 10% after about two hours(Fig. 1, case A) accompanied by fading of the color.[6] From the reaction mixture, magnesium benzoate and *trans*-1,2-dibromocyclohexane were obtained almost quantitatively. When anhydrous THF solution of $MgBr_2$ was added to the mixture of BPO and cyclohexene dissolved in THF(Fig. 1, case B), the peroxide-content decreased immediately. The reaction was slow and a longer time was needed for it to be completed, the products being the same as those in case A. The two curves in Fig. 1 show that Complex III liberates the first bromine atom on access of olefin molecule (Reaction 3).

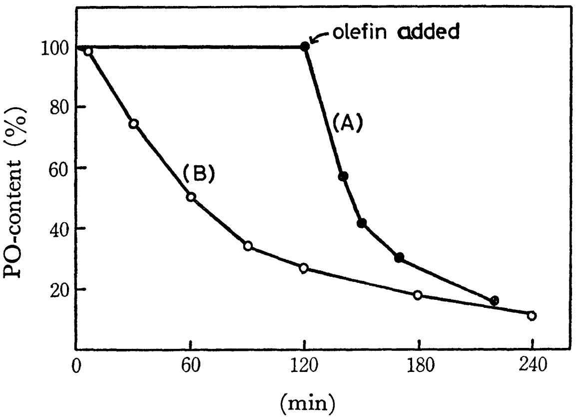
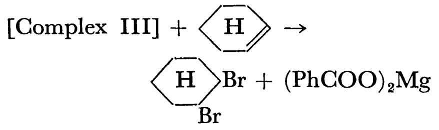
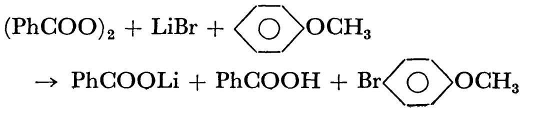


Fig. 1. Consumption of BPO-content at 20 °C.
Concn: 0.0042 mol in 100 ml THF.
Curve A: After 2 hr, olefin is added to Complex III.
Curve B: $MgBr_2$ is added to the mixt. of BPO and olefin.



(3)

Kochi and his co-workers reported the formation of *p*-bromoanisole in the reaction of lithium bromide with BPO in a mixture of acetic acid and anisole[7] (Reaction 4).



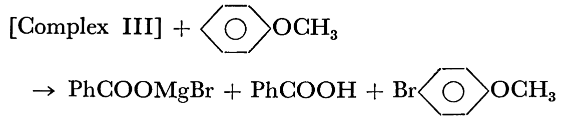
(4)

Table 1. Reaction of case B at 20 °C
Concentration: 0.0042 mol in 100 ml THF.

Time (s)	P. O.-content consumed (%)	Rate consts. calcd. on 1st-order eq.[a] (s^{-1}) $\times 10^4$	2nd-order eq. ($l \cdot mol^{-1} \cdot s^{-1}$) $\times 10^3$	3rd-order eq. ($l^2 \cdot mol^{-2} \cdot s^{-1}$) $\times 10^1$
480	3.2	0.68	1.63	0.39
1740	22.5	1.46	3.95	1.07
3420	46.4	1.82	6.00	2.04
4320	58.0	2.01	7.58	3.03
5520	66.6	1.99	8.56	4.05
7020	72.5	1.84	8.90	4.89

a) The latter four numbers were used to calculate the mean value of the apparent-first-order rate constant.

An equimolar mixture of Complex III and anisole in THF at 25 °C slowly gave *p*-bromoanisole(Reaction 5).



(5)

This suggests that anisole as well as cyclohexene abstract brominium cation from Complex III in reactions 5 and 3, respectively.

The possibility that Complex III consists of benzoyl hypobromite and benzoyloxymagnesium bromide(Reaction 6), could be excluded since no Hunsdiecker-Prévost-type product such as 2-bromocyclohexyl benzoate[8] was detected in cases A and B.

$$(PhCOO)_2 + MgBr_2 \rightarrow [PhCOOBr][PhCOOMgBr] \quad (6)$$

Since Complex III no longer has characteristic infrared absorption bands of BPO itself,[9] it cannot be pictured as a simple mixture of $MgBr_2$ and BPO. If the structure of Complex III were to be depicted, the Mg-Br bond and O–O bond might be said to have excited characters. Bromine atom may have a positive charge as the result of coordination of electron-seeking peroxide molecules to the Mg-atom. This is justified by the formation of *p*-bromoanisole. Complex III liberates bromine when it is treated with water.[5]

Since a straight line was obtained when the olefin had not yet been added(Fig. 1, case A) and no appreciable fluctuation which we came across in the lithium bromide–BPO system[7] was not observed(Fig. 1, case B), the features of decomposition of Complex III could be followed by iodometry. Typical results of measurements in case B are listed in Table 1. The first-order rate constants show a smaller fluctuation as compared with the other two series of values. The apparent-first-order rate constants remained virtually unchanged when two molar equivalents of cyclohexene were used. $MgBr_2$ in slight excess, however, greatly accelerates the reaction as shown in Fig. 2. In case A, no satisfactory rate constant was obtained by using any of the first-, second- and third-order rate equations. This might be due to the change of degree of association(or dissociation) of Complex III(Reaction 2) caused by the change in concentration. Addition of olefin-THF solution at the initial stage of case A alters the concentration at that time, affecting the rate of decomposition of Complex III. The overall path of reaction should thus consist mainly of i) equilibrium(2), and ii) abstraction of brominium cation from Complex III to form 2-bromocyclohexyl carbonium ion, which may combine rapidly with the bromide ion in the subsequent step.

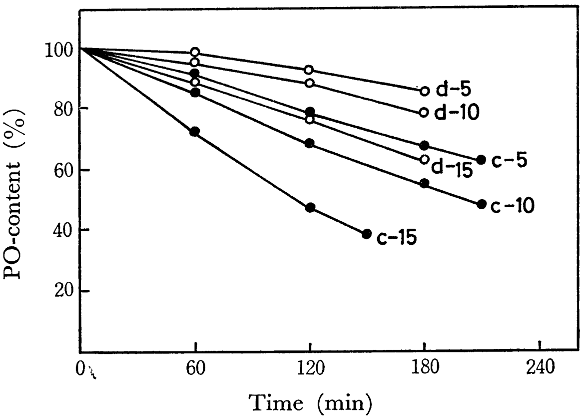


Fig. 2. Consumption of BPO-content (case B).
Effect of temperature and $MgBr_2$-concentration.
i) Concn. of BPO and cyclohexene are fixed to 0.00238 mol in 45 ml THF. ii) Numbers (5, 10 and 15) denote the temperature (°C). iii) "c" and "d" denote the concn. of $MgBr_2$-soln (15 ml). c: 0.173 M, d: 0.159 M.

Effects of the substituent of BPO and the structure of olefin were examined mainly for case B. *p,p'*-Dinitrobenzoyl peroxide greatly accelerates the reaction which completed within 20 min. at 20 °C (Table 2, and Fig. 3-a, b). Since the species abstracted by the π-electron system of cyclohexene should be brominium cation, the facilitation of this step by the electron-attracting substituent is reasonable.[10] We see from Fig. 3-b and 3-c that the difference between the rate of BPO and that of *m,m'*-dimethoxy derivative decreases with the lowering in temperature. Weakly electron-attracting *m*-methoxy group should be less favorable to complex-formation(Reaction 2). The tendency might become greater at a higher temperature; thus, the overall rate of *m,m'*-dimethoxy derivative becomes relatively lower(Fig. 3-b). Both equilibrium(2) and the rate of abstraction of bromi-

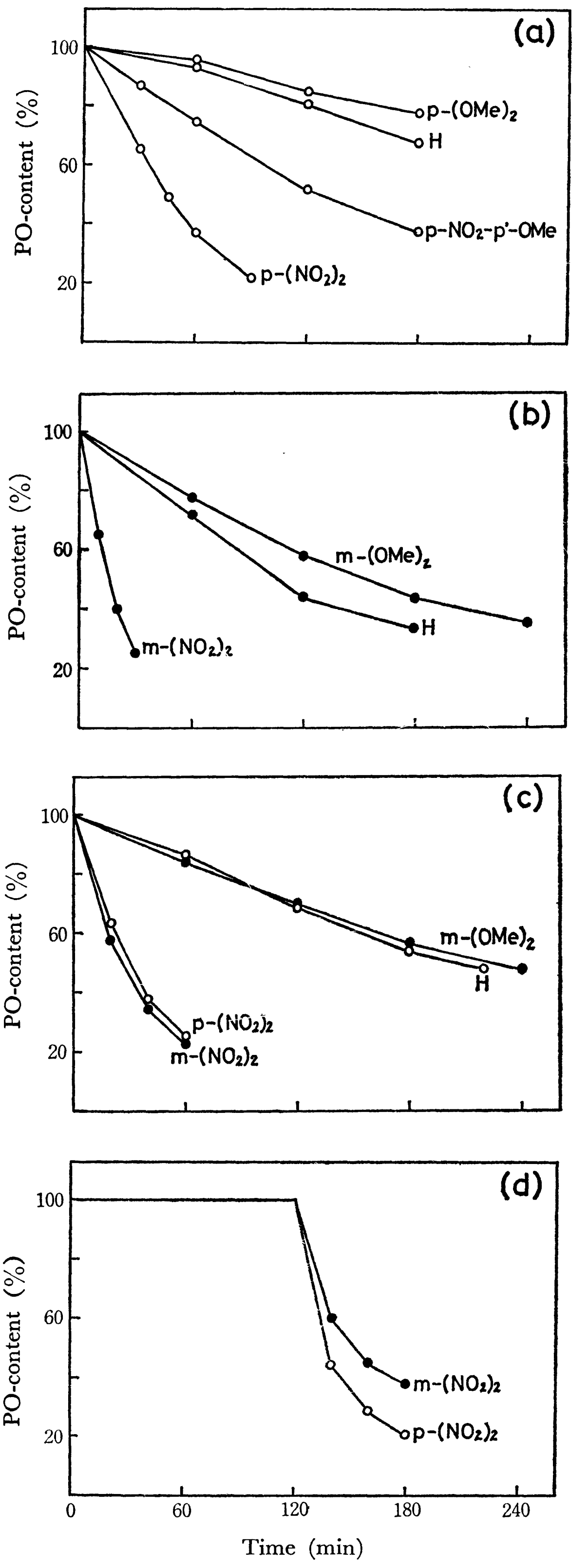


Fig. 3. Comsumption of PO-content for cases A and B. a) case B, 15 °C, *p*-substituted BPO, $MgBr_2$: 0.159 M. b) case B, 15 °C, *m*-substituted BPO, $MgBr_2$: 0.173 M. c) case B, 10 °C, *p*- and *m*-substituted BPO, $MgBr_2$: 0.173 M. d) case A, 5 °C, *p*- and *m*-nitro derivatives, $MgBr_2$: 0.173 M.

Concn of peroxides and cyclohexene are to 0.00238 mol in 45 ml THF.

TABLE 2. APPARENT-FIRST-ORDER RATE CONSTANTS FOR SUBSTITUTED BPO IN REACTION WITH CYCLOHEXENE AT 20 °C (case B)

Concentration: 0.0042 mol in 100 ml.

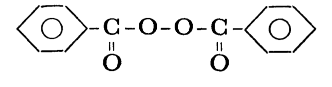
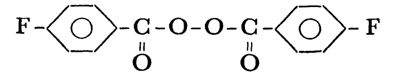
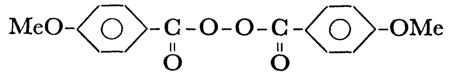
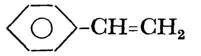
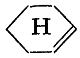
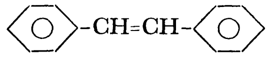
Peroxides	Rate constant (s^{-1}) $\times 10^4$
	1.9
	2.4
	0.8

TABLE 3. APPARENT-FIRST-ORDER RATE CONSTANTS FOR OLEFINS IN REACTION WITH BPO AT 20 °C (case B)

Concentration: 0.0042 mol in 100 ml.

Olefins	Rate constant (s^{-1}) $\times 10^5$
t-Bu-CH=CH$_2$	1.4
CH_3-($-CH_2-$)$_5$-CH=CH$_2$	3.2
	2.8
	19.0
	Very slow

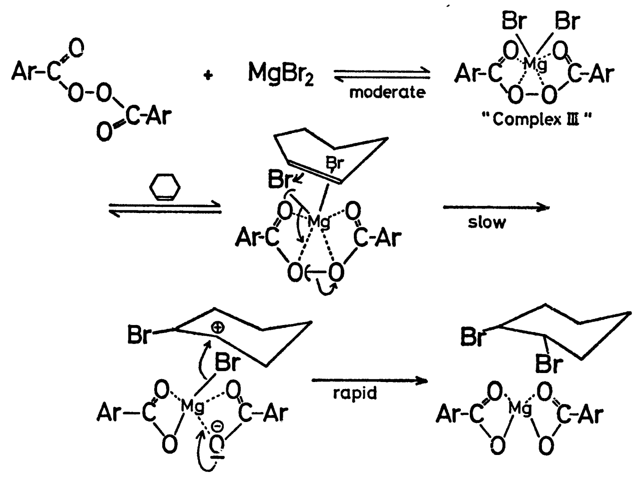
nium cation by the olefinic system should change with temperature and substituent. Lower temperature and an electron-donating substituent favor the association of Complex III; higher temperature and an electron-attracting substituent favor the abstraction of brominium cation. At 10 °C, *m,m'*-dinitro-derivative decomposed at a rate somewhat higher than that for *p,p'*-derivative(Fig. 3-c). In case A at 5 °C, however, the *p,p'*-derivative decomposed much faster than the *m,m'*-derivative(Fig. 3-d). Thus the *m*-nitro group should be more favorable to the association of Complex III than the *p*-nitro group; the *p*-nitro group accelerates the abstraction of brominium cation to a greater extent than the *m*-nitro group.

Apparent-first-order rate constants(case B) for several olefins were obtained when unsubstituted BPO was used (Table 3). The rate decreases in the following order:

cyclohexene > 1-octene > styrene > *t*-butylethylene >
cis-stilbene > *trans*-stilbene.

The rate of *trans*-stilbene at room temperature is so low that the peroxide-content was consumed after about 30 days. The rate of *cis*-isomer was as high as twice that of *trans*-isomer. π-Electron density of the ethylene groups of stilbenes and styrene is lower than that of alkyl-substituted ethylenes owing to delocalization of electrons on the whole of molecule, and might be unfavorable to the abstraction of brominium cation. Bulkiness of the phenyl and *t*-butyl groups may also be another retarding factor. The fact that cyclohexene reacts very fast and that *cis*-stilbene reacts faster than *trans*-isomer shows that the olefins having *cis*-type configuration favor the reaction.

The course of the reaction in the case of cyclohexene could be formulated as follows:



Experimental

Materials. A clear solution of $MgBr_2$(about 0.2 M) in anhydrous THF was prepared from Mg-turnings and ethylene dibromide.[4] Its concentration was determined by the magnesium-oxinate method.[11] When necessary benzoyl peroxide was purified by reprecipitation with methanol from its chloroform solution. *p,p'*-Difluoro-, *p,p'*-dimethoxy-, *m,m'*-dimethoxy-, *p,p'*-dinitro- and *m,m'*-dinitro-benzoyl peroxides were prepared from the corresponding acyl chlorides and peroxide.[12] *p*-Nitro-*p'*-methoxybenzoyl peroxide was prepared by the condensation of *p*-nitroperoxybenzoic acid and *p*-anisic acid with dicyclohexylcarbodiimide.[13] Cyclohexene and styrene were purified by distillation before use. *trans*- and *cis*-Stilbene were prepared from *trans*- and *cis*-α-phenylcinnamic acids, respectively.[14] *t*-Butylethylene was prepared from pinacolone by reduction and dehydration by means of the methylxanthate method.[15]

Rate Measurements. A typical procedure for case B is described in the following. Anhydrous THF(60 ml) was introduced into the N_2-purged reaction flask at 20 °C and 1.0113 g (0.0042 mol) of BPO was added. Cyclohexene (0.346 g, 0.0042 mol) dissolved in 10 ml THF was added to the solution. Twenty milliliters of $MgBr_2$ solution (0.211 M) and 10 ml THF were successively introduced into the reservoir,[16] and the apparatus was set up under a slow stream of nitrogen. The mixture in the reaction flask was vigorously stirred and the $MgBr_2$ solution was added at once by turning the reservoir upside-down. After mixing, the total volume of the reaction mixture was 100 ml. One milliliter portions of the reaction mixture were pipetted out at definite intervals, introduced into a CO_2-purged flask containing acetic acid and potassium iodide, and titrated.[17]

For case A, BPO and $MgBr_2$ were mixed in THF under N_2-atmosphere. The reaction flask was kept in a water bath controlled at a definite temperature for over 8 hr, when the solution turned orange. Cyclohexene dissolved in 10 ml THF was added at once, and the peroxide-content was followed by iodometry.

Analysis of Products. After the peroxide-content became zero, the reaction mixture was concentrated under reduced pressure to a small volume, decomposed by saturated ammonium chloride solution, extracted with ether and worked up as usual. Benzoic acid was obtained quantitatively. From the neutral part, *trans*-1,2-dibromocyclohexane was obtained in 82—90% yields. 2-Bromocyclohexyl benzoate was prepared[8] and used for comparison with the products of this reaction on tlc. The yield of dibromide was determined on vpc using hexachloroethane as an internal reference. The conformation of the dibromide was identified by comparing its retention time on vpc with that of the dibromide prepared by adding bromine to cyclohexene in CCl_4.[18]

p-Nitro-*p'*-methoxybenzoyl peroxide is known to decompose with ionic mechanism *via* carboxy-inversion.[19] However, in our reaction no *p*-methoxyphenol was detected.

Electrophilic Bromination. A solution of Complex III was prepared from 0.726 g (0.003 mol) of BPO and equimolar $MgBr_2$ solution (total volume: 60 ml). Anisole(0.324 g) dissolved in 10 ml THF was added. After the mixture was stirred at 25 °C for 6 hr, the peroxide-content fell to 69%. The yield of *p*-bromoanisole was determined to be 13% on vpc.

The authors are grateful to Professor Kazuhiro Maruyama, Kyoto University, for his stimulating discussions.

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6) The curve, obtained in the case when cyclohexene was added to the solution of Complex II, was nearly the same as curve A.

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9) Infrared absorption bands(in THF) of C=O stretching vibration shifted from 1770 cm^{-1} in the case of free BPO to 1640 cm^{-1} in that of Complex III.

10) Considering this and the results described later, we can exclude the other possibility that Complex III is a molecular compound in which molecular bromine is adsorbed on magnesium benzoate.

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