N-Bromosuccinimide. Mechanisms of Allylic Bromination and Related Reactions[1]

J. H. Incremona[2] and J. C. Martin

Contribution from the Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801. *Received June 23, 1969*

Abstract: The near-identity of the selectivities of molecular bromine, N-bromosuccinimide (NBS), and N-bromotetramethylsuccinimide (NBTMS) obtained from competitive allylic bromination studies provides strong evidence that the operative mechanism in NBS allylic bromination is one involving Br· as the chain-carrying species. The NBS acts to provide a low steady-state concentration of Br_2 in a mechanism similar to that (originally suggested by Goldfinger) which has been established for benzylic bromination reactions. The selectivity shown in benzylic bromination with N-bromotetrafluorosuccinimide (NBTFS) is identical with that of NBS (or Br_2). In the allylic bromination of olefins containing electron-rich double bonds, on the other hand, NBTFS shows a selectivity significantly greater than that of NBS (or Br_2). This variance in selectivity is attributed to the importance of an ionic pathway available to NBTFS for the formation of allylic bromides. Evidence is presented supporting this postulate.

Since Ziegler's[3] study of the synthetic utility of N-bromosuccinimide (NBS) as a brominating agent, there has been considerable question concerning the mechanism(s) of NBS allylic and benzylic bromination. Among the mechanisms proposed, those of Bloomfield[4] and Goldfinger[5,6] have seemed the most plausible. Both mechanisms satisfy the experimentally derived rate expression for the NBS allylic bromination of cyclohexene as obtained by Youngman and Dauben.[7]

Bloomfield Mechanism[a]

$$I\cdot + SNBr \longrightarrow SN\cdot + IBr$$

$$SN\cdot + RH \longrightarrow R\cdot + SNH \quad (1)$$

$$R\cdot + SNBr \longrightarrow SN\cdot + RBr \quad (2)$$

$$2SN\cdot \longrightarrow \text{nonradical products}$$

Goldfinger Mechanism[a]

$$I\cdot + Br_2 \longrightarrow IBr + Br\cdot$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot \quad (3)$$

$$HBr + SNBr \longrightarrow Br_2 + SNH \quad (4)$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \quad (5)$$

$$2Br\cdot \longrightarrow Br_2$$

[a] SNBr and SNH are N-bromosuccinimide and succinimide, respectively, and I· is initiator radical.

For many years, the attractive simplicity of the Bloomfield mechanism, complemented by the results of various selectivity studies,[8] led to a general acceptance of the succinimidyl radical process as the operative mechanism both for allylic and benzylic bromination. In more recent years, however, independent investigations in three laboratories[9-12] have provided strong support for the Goldfinger mechanism.

Several lines of research[13] have suggested that the generation of succinimidyl radicals may be quite a difficult process and serve to provide a rationale for the otherwise surprising failures to observe the operation of the Bloomfield mechanism. It has recently been suggested,[14] however, that the Bloomfield mechanism is operative in the N-iodosuccinimide oxidation of alcohols.

Other studies suggest that the Goldfinger proposal may be operative in NBS aliphatic and allylic bromination. In this regard, Skell, Tuleen, and Readio[15] have observed the bromination of (+)-1-bromo-2-methylbutane *via* molecular bromine or NBS to afford exclusively 1,2-dibromo-2-methylbutane *via* a mechanism postulated to involve bridged bromonium radicals. Interestingly, when the bromination was conducted with molecular bromine under high dilution, the observed optical rotation of the product was similar to that afforded with NBS. These findings were interpreted in terms of a mechanism for NBS aliphatic bromination in which the function of the NBS is to provide a low, steady-state concentration of bromine (step 4). For the case of allylic bromination, independent studies by Tedder and McGrath[16] and Sixma and Riem[17] demonstrate decisively that the substitution reaction can be achieved using molecular bromine if the concentration of the bromine is maintained low and constant. Erratic or rapid addition of bromine to the reaction medium leads to increased dibromide formation and low yields of allylic bromide.

(1) Presented as a part of the Symposium on Free Radical Chemistry, 149th Meeting of the American Chemical Society, Detroit, Mich., 1965, Abstract p 16.
(2) Abstracted from the Ph.D. Thesis of J. H. I., University of Illinois, 1966.
(3) K. Ziegler, A. Speath, E. Schaaf, W. Schamann, and E. Winkelmann, *Ann.*, 551, 80 (1942).
(4) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).
(5) J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, 171, 704 (1953).
(6) J. Adam, P. A. Gosselain, and P. Goldfinger, *Bull. Soc. Chim. Belges*, 65, 523 (1956).
(7) E. A. Youngman, Ph.D. Thesis, University of Washington, Seattle, Wash., 1952.
(8) E. C. Kooyman, R. Van Helden, and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, B56, 75 (1953).
(9) R. E. Pearson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.
(10) J. C. Martin and R. E. Pearson, *J. Am. Chem. Soc.*, 85, 354, 3142 (1963).
(11) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, 85, 365 (1963); G. A. Russell and K. M. Desmond, *ibid.*, 85, 3139 (1963).
(12) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, 85, 3129 (1963); C. Walling and A. L. Rieger, *ibid.*, 85, 3134 (1963).
(13) (a) T. Koenig and W. Brewer, *ibid.*, 86, 2729 (1964); (b) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *ibid.*, 89, 4875 (1967).
(14) T. R. Beebe and F. M. Howard, *ibid.*, 91, 3379 (1969)
(15) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, 85, 2849 (1963).
(16) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).
(17) F. L. J. Sixma and R. H. Riem, *Koninkl. Ned. Akad. Wetenschap. Proc.*, B61, 183 (1958).

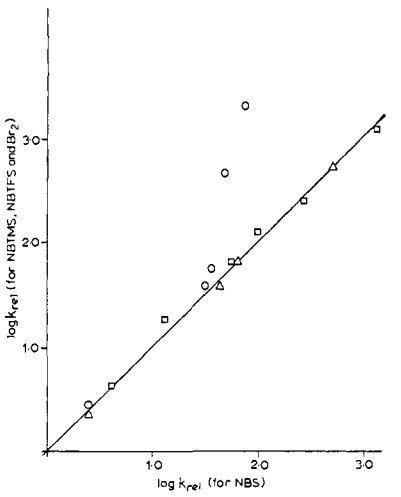
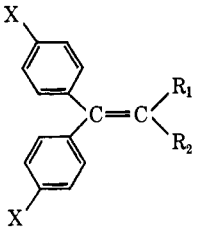


Figure 1. Comparison of the relative reactivities of olefins in allylic bromination by NBS with those for bromination by NBTMS (△), NBTFS (○), or Br_2 (□). The solid line has a slope of 1.

Despite the implications of these experiments, it would be premature to assume the Goldfinger sequence to be operative in the mechanism for NBS allylic bromination. Many examples are known in which the presence of olefins drastically alters the rates or courses of radical processes.[13,18,19] The allylic double bond could, by forming complexes with chain-carrying radicals, change the course of the reaction from that observed for benzylic bromination.

In view of the uncertain situation, a study intended to elucidate the mechanism of NBS allylic bromination was undertaken. Our experimental approach was similar to that described by Martin and Pearson,[9] and involved a comparison of the selectivities of various brominating agents as obtained from competitive allylic bromination studies. The brominating agents used were NBS, N-bromotetramethylsuccinimide (NBTMS), N-bromotetrafluorosuccinimide (NBTFS), and molecular bromine. Our assumption that these differently substituted succinimidyl radicals would show differing selectivities in reactions in which they serve as hydrogen-abstracting species has been defended earlier.[9]



1a, X = OCH_3; $R_1 = R_2 = CH_3$
b, X = *t*-butyl; $R_1 = R_2 = CH_3$
c, X = H; $R_1 = C_6H_5$; $R_2 = CH_3$
d, X = H; $R_1 = R_2 = CH_3$
e, X = H; $R_1 = CH_3$; $R_2 = H$
f, X = Cl; $R_1 = R_2 = CH_3$
g, X = Br; $R_1 = R_2 = CH_3$
h, X = CN; $R_1 = R_2 = CH_3$
i, X = *t*-butyl; $R_1 = R_2 = CD_3$

(18) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, 85, 1593, 1597 (1963).
(19) C. Walling and P. Wagner, *ibid.*, 85, 2333 (1963).

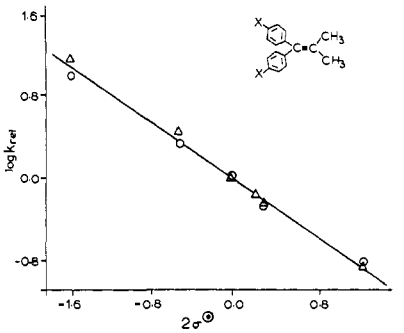


Figure 2. Bromination of olefins at 25° in benzene with NBS (points indicated by △) and bromine (points indicated by ○).

The substrates used in these brominations included, in order of decreasing reactivity, a series of *para*-substituted 1,1-diarylpropenes (**1a** > **1b** > **1c** > **1d** > **1e** > **1f** > **1g** > **1h**), methyl α-methylcinnamate (**2**), toluene (**3**), and *m*-bromotoluene (**4**). A deuterated substrate (**1i**) and *p*-xylene (**5**) were also used for some experiments.

Results and Discussion

Rate Studies. Reactions were usually carried out at 80 or 25°, and were initiated using azobisisobutyronitrile, benzoyl peroxide, and/or ultraviolet light. The substrates chosen for any run were such as to allow ready analysis by nmr spectroscopy. The quantities of product bromides formed were measured by direct comparison with an internal standard. Results from which relative rates are determined are compiled in Table I.

Material balance was established in all reactions involving NBS or NBTMS. For reactions involving molecular bromine, 92% or more of the olefinic substrates could be accounted for as either unreacted starting materials or product bromides. In the case of NBTFS, it was noted that, in general, the yields of product bromides did not exceed 75%. The importance of nuclear substitution in some cases could account, either partially or totally, for the low yields observed. For example, the reaction of NBTFS with 1,1-bis(*p*-methoxyphenyl)-2,2-dimethylethylene (**1a**) afforded little if any of the expected allylic bromide. A gas which was evolved from the reaction medium was presumed to be hydrogen bromide. It seems improbable, however, that nuclear substitution could be of much importance in reactions involving olefins such as methyl α-methylcinnamate (**2**) or 1,1-bis(*p*-bromophenyl)-2,2-dimethylethylene (**1g**). It is likely that, for these cases, NBTFS is consumed in a process not involving the substrates. A similar observation was reported by Pearson[9] in a study of the reaction of NBTFS with *t*-butyltoluene. After total disappearance of the brominating agent, a material balance could be established for the substrate but not for the brominating agent.

Table II and Figure 1 present relative rates of proton abstraction for the various brominating agents. The excellent correlation of certain of our data in a Hammett $\sigma\rho$ treatment is shown in Figure 2. The least-squares values of ρ for Br_2 (−0.70, correlation coefficient 0.9988), for NBS (−0.75, 0.9991), and for all the data for both reagents considered together (−0.72, 0.9966) are very nearly identical. The near identity of

Table I. Relative Rates from Competitive Brominations[a]

Run no.	Brominating agent	T, °C	% reaction	Reactant A			Reactant B			k_{rel}[b]
				Compd	A	X	Compd	B	Y	
1	NBS	50	98	**1a**	0.731	0.442	**1c**	2.587	0.115	7.96
2	NBS	80	78	**1e**	0.484	0.262	**2**	2.636	0.108	18.7
3	NBS	80	100	**1c**	0.704	0.326	**3**	11.48	0.100	71.0
4	NBS	80	98	**2**	1.093	0.209	**3**	3.768	0.296	2.59
5	NBS	80	98	**2**	1.263	0.226	**3**	4.163	0.321	2.46
6	NBS	80	100	**1c**	0.936	0.434	**1d**	0.591	0.384	1.58
7	NBS	80	78	**1d**	0.666	0.340	**3**	44.15	0.260	51.2
8	NBS	80	81	**1d**	1.050	0.248	**1f**	0.984	0.152	1.57
9	NBS	80	102	**1b**	0.457	0.162	**1d**	1.575	0.374	1.61
10	NBS	80		**1g**	0.646	0.197	**3**	44.42	0.208	34.2
11	NBS	25		**1a**	0.414	0.182	**1g**	3.186	0.072	25.3
				1d	3.168	0.131	**1g**	3.186	0.072	1.84
12	NBS	25		**1a**	0.455	0.230	**1g**	9.063	0.248	25.3
				1d	3.303	0.156	**1g**	0.063	0.248	1.74
13	NBS	25	104	**1b**	0.720	0.310	**1f**	1.803	0.232	4.08
14	NBS	25		**2**	1.004	0.256	**3**	3.989	0.265	4.27
15	NBS	25		**1g**	0.504	0.344	**2**	2.542	0.073	14.3
16	NBS	25		**1g**	0.490	0.219	**3**	51.87	0.210	59.4
17	NBS	25		**1g**	0.454	0.207	**1h**	1.202	0.158	4.32
18	NBTMS	50	96	**1a**	0.655	0.408	**1c**	2.369	0.105	8.23
19	NBTMS	80	80	**1e**	0.685	0.426	**2**	2.617	0.146	17.0
20	NBTMS	80	91	**1c**	0.704	0.320	**3**	11.48	0.097	69.2
21	NBTMS	80	92	**2**	1.059	0.178	**3**	4.011	0.300	2.37
22	NBTFS	80	76	**1c**	0.584	0.319	**3**	9.082	0.073	98.0
23	NBTFS	80	76	**1c**	0.853	0.366	**3**	12.04	0.047	135.2
24	NBTFS	80	76	**1c**	0.598	0.298	**3**	12.66	0.079	111.0
26	NBTFS	80	70	**2**	1.148	0.166	**3**	4.067	0.226	2.72
27	NBTFS	80	81	**2**	0.9605	0.153	**3**	3.904	0.217	3.04
28	NBTFS	80	81	**1c**	0.830	0.081	**1d**	0.667	0.300	2.49
29	NBTFS	80	74	**1d**	0.648	0.270	**1f**	1.053	0.067	8.20
30	NBTFS	80	91	**1d**	0.456	0.280	**1f**	1.435	0.147	8.80
31	NBTFS	80	83	**1f**	0.546	0.252	**3**	37.65	0.160	59.9
32[c]	NBTFS	80	70	**1g**	0.443	0.116	**3**	48.79	0.170	40.6[c]
33	NBTFS	80		**1b**	0.530	0.086	**1d**	4.172	0.162	4 47
34	NBTFS	80		**1b**	0.461	0.209	**1f**	3.151	0.170	10.9
35[d]	NBTFS	80	74	**1g**	0.561	0.263	**3**	44.07	0.078	166[d]
36[e]	NBTFS	80	54	**1g**	0.573	0.200	**3**	46.03	0.063	167[e]
38	NBTFS	80	92	**5**	13.38	0.082	**3**	104.2	0.089	3.25
				1d	0.595	0.247	**3**	104.2	0.089	253
39	Br_2	25	103	**1a**	0.737	0.315	**1g**	7.482	0.212	19.5
			103	**1a**	0.737	0.315	**1d**	2.843	0.154	9.99
			103	**1d**	2.843	0.154	**1g**	7.482	0.212	1.95
40	Br_2	25		**1a**	0.829	0.303	**1g**	7.568	0.234	14.3
41	Br_2	25	86	**1b**	0.494	0.174	**1g**	0.921	0.093	4.07
			86	**1b**	0.494	0.174	**1d**	0.871	0.168	2.03
			86	**1d**	0.871	0.168	**1g**	0.921	0.093	2.00
42	Br_2	25	78	**1g**	0.501	0.294	**2**	2.877	0.069	14.4
43	Br_2	25	70	**1g**	0.744	0.391	**2**	3.196	0.060	16.2
44	Br_2	25		**1g**	0.507	0.256	**2**	2.843	0.047	17.3
45	Br_2	25		**1b**	0.658	0.138	**1g**	1.954	0.140	3.17
				1d	1.558	0.184	**1g**	1.954	0.140	1.69
46	Br_2	25	83	**1g**	0.501	0.276	**1h**	0.886	0.174	3.66
47	Br_2	25		**2**	1.217	0.318	**4**	11.94	0.160	22.6
48	Br_2	25	66	**2**	1.123	0.183	**4**	9.910	0.089	19.3
49	Br_2	25	60	**2**	1.057	0.244	**4**	9.162	0.110	21.5
50[f]	Br_2	25	72	**1i**	0.484	0.195	**5**	13.24	0.110	62.2
51[f]	Br_2	25	44	**1b**	0.210	0.061	**1i**	0.072	0.011	2.07

[a] Brominations of mixtures of two, three, or four substrates were carried out in benzene to the indicated degree of completion (based on loss of the brominating agent) by a procedure described in the Experimental Section. The concentrations of the more reactive substrate A and its bromination product X, the less reactive substrate B and its bromination product Y, were determined by nmr at the end of the reaction. The amounts of these compounds (in mmoles) are listed in the appropriate columns. [b] $k_{rel} = [\log (A - X)/A]/[\log (B - Y)/B]$. [c] No initiator added. [d] Diphenylpicrylhydrazyl (0.05 mmole) added to medium; no initiator present. [e] Diphenylpicrylhydrazyl (0.05 mmol) added to medium; benzoyl peroxide added. [f] Ratios of concentrations determined mass spectrometrically. In run 50 compound **1b** was added after reaction as an internal standard.

selectivities for three of the four brominating agents (Br_2, NBS, and NBTMS) is clearly demonstrated in Figure 1. The selectivity shown by NBTFS is, however, very different for reactions involving olefins of relatively high electron density. As will be shown in later discussion this difference in selectivity is attributable to the importance of an ionic pathway available to NBTFS for the formation of allylic bromides.

It has been demonstrated[9,10,20] that for benzylic photobrominations by molecular bromine, the hydrogen abstraction step is reversible. In the benzylic studies[9,10] this reversal was minimized by swamping the reaction medium with such a large excess of bromine that at all stages of reaction the molar ratio of Br_2 to HBr

(20) K. B. Wiberg and L. H. Slaugh, *J. Am. Chem. Soc.*, 80, 3033 (1958).

Table II. Relative Rates of Bromination of Olefins

Substrate	Brominating agent: NBS (80°)	NBTMS (80°)	NBS (25°)	Br_2 (25°)	NBTFS (80°)
3	1.00	1.00	1.00	1.00	1.00
2	2.53 (**3**)[a]	2.37 (**3**)	4.27 (**2**)	4.36[b]	2.88 (**3**)
1e	47.3 (**2**)	40.3 (**2**)			
1c	71.0 (**3**)	69.2 (**3**)			
1h			14.2 (**1g**)	19.1 (**1g**)	
1g	34.2 (**3**)		61.1 (**2**)	69.8 (**2**)	40.6 (**3**)
1f	38.7 (**3**)		74.0 (**1b**)		59.9 (**3**)
1d	51.2 (**3**)		109.4 (**1g**)	131.2 (**1g**)	509.2 (**1f**)
1b	82.4 (**1d**)		301.9 (**1d**)	266.3 (**1d**)	2276.1 (**1d**)
1a	565.2[c] (**1c**)	569.5[c] (**1c**)	1545.8 (**1g**)	1312 (**1g**)	Nuclear subst

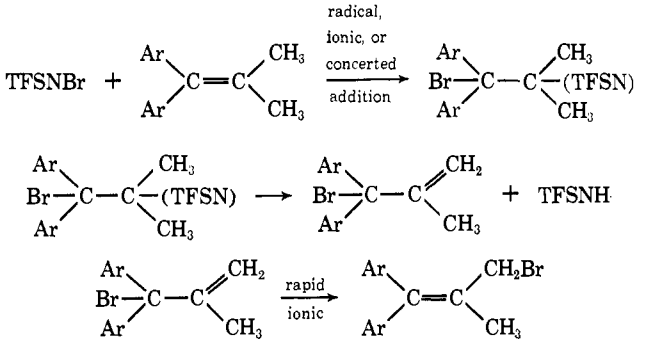
[a] Numbers in parentheses indicate the intermediary compounds used in calculating the specified relative reactivities. [b] Calculated from the relative rate constants obtained for the systems methyl α-methylcinnamate–*m*-bromotoluene (k_{rel} = 21.1) and toluene–*m*-bromotoluene (k_{rel} = 4.83). The value for the latter value is taken from ref 6. [c] Relative rate constants for the system X = OCH_3, $R_1 = R_2 = CH_3$–methyltriphenylethylene were obtained at 50°.

was no less than 50. Such a technique is precluded in this study of olefinic substrates to which bromine would be expected to add rapidly. We therefore used the alternative approach of removing hydrogen bromide by sweeping it away in a rapid stream of nitrogen bubbled through the reaction mixture. The near identity of the selectivities of Br_2 and NBS (Table I) suggests that the approach was successful in minimizing reversibility of the hydrogen abstraction step. This was confirmed by carrying out competitive brominations employing as one of the competing substrates the deuterated olefin, 1,1-bis(*p*-*t*-butylphenyl)-2,2-dimethyl-d_6-ethylene. By comparing the relative quantities of olefin-d_6 and olefin-d_5h before and after reaction, the percentage of reversal in the hydrogen abstraction step was shown not to exceed 10%. Only a small distortion of the relative reactivity scale would be introduced by an incursion of this reaction between allyl radicals and hydrogen bromide to the extent of no more than 10%. Rate constant ratios (k_A/k_B) were calculated to be increased 1–10% in typical runs from Table I assuming this reversal to be important only for the more reactive substrate. Since consideration of such a reverse reaction places an upper limit on the size of the correction which is comparable in magnitude to our experimental error, the values here reported for relative reactivities have not been corrected for this minor perturbation. Those few cases in which relative reactivities toward bromine and NBS differ by an amount greater than the experimental error of our analyses (for example, runs 12 and 40) are not, therefore, different because of the importance of this reaction in the bromination with Br_2. On the basis of these results we conclude that the relative reactivities obtained in those competitive runs using molecular bromine accurately reflect the relative rates of proton abstraction from the substrates by the attacking bromine atom. We conclude further that the near identity of the selectivities of NBS, NBTMS, and Br_2, as demonstrated in the previous figures and tables, provides strong evidence that the operative mechanism for NBS allylic bromination involves, at least for the substrates studied here, the bromine atom as the chain-carrying species (the Goldfinger mechanism). The possibility of alteration of the mechanism by formation of complexes between chain propagating radicals and the electron rich double bond, which could not be excluded *a priori*, has apparently not changed the major chain propagating sequence from that seen for benzylic bromination. It had already been shown[13] that the relative reactivities of substituted toluenes toward NBS were uninfluenced by the presence of olefins in the reaction medium.

The Reactions of N-Bromotetrafluorosuccinimide with Olefins. The selectivity of NBTFS was observed to be consistently greater than that of NBS or NBTMS in reactions with olefins of relatively high electron density (Tables I and II, Figure 1). This difference in selectivity strongly implies a difference in mechanism, *i.e.*, that there are at least two pathways by which NBTFS can react with some olefins to afford high yields of allylic bromides. As has already been discussed, one of these pathways, the Goldfinger mechanism, is probably operative for the olefins of low electron density (the points falling on the line of Figure 1).

Other plausible reaction pathways include the Bloomfield mechanism (which might, in reactions with electron-rich substrates, be favored by the electrophilicity[21] of the tetrafluorosuccinimidyl radical) and that of Scheme A, involving initial addition to the double bond. The addition reaction of Scheme A, whether radical,[22]

Scheme A



ionic, or cyclic concerted, might be expected to be favored by the electron-withdrawing inductive effect of the fluorine substituents of TFNBS.

Several runs tabulated in Table I provide data which are significant with respect to the mechanism of this reaction. Earlier work[10] had shown xylene to be 3.22

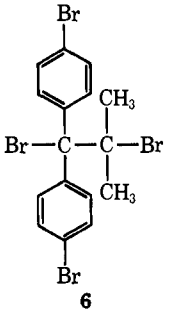
(21) Radical chain processes presumably involving H abstraction by the electronegative protonated succinimidyl radical have been reported by D. D. Tanner, *J. Amer. Chem. Soc.*, **86**, 4674 (1964).

(22) The radical addition of NBS to olefins lacking α-hydrogens has been reported: L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, 29, 1290 (1964). See also S. Wolfe and D. U. C. Awang, *J. Am. Chem. Soc.*, 89, 5287 (1967).

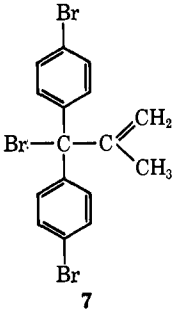
times more reactive than toluene toward bromine atom in benzene at 80°. In run 38 we find the comparable rate ratio to be 3.25 in a medium containing the electron-rich olefin **1b**. The presence of this olefin has, therefore, not shifted the course of this benzylic bromination to the Bloomfield mechanism, confirming a related earlier observation.[13]

In runs 10 and 32c the selectivities of NBS and NBTFS are seen to be closely similar in competitive brominations of toluene and olefin **1g** (relative rates 34.2 and 40.6). In runs 35 and 36, the addition of the inhibitor DPPH results in an increase to 166 or 167 in the measured relative reactivity of the olefinic substrate toward allylic bromination by NBTFS. This suggests that the free-radical bromination of run 10 or the predominantly free-radical reaction of run 33 is inhibited by the DPPH, allowing the more selective competing nonradical allylic bromination to proceed and greatly increasing the measured selectivity. The difference between 40.6 (NBTFS, run 33) and 34.2 (NBS, run 10) results from the operation of about 20% of the nonradical allylic bromination by NBTFS in run 33. This rules out the possibility that free-radical chain mechanisms are the only ones important for this brominating agent.

Spectroscopic evidence for the intermediacy of the adduct of Scheme A is obtained by mixing solutions of NBTFS and olefin **1g** in the dark at room temperature and following the progress of the reaction by ^1H or ^{19}F nmr spectroscopy. In solvents benzene, carbon tetrachloride, and chloroform-*d* one notes the disappearance, too rapid to follow, of the δ 1.77 peak, assigned to the six allylic protons of the **1g** methyl groups, and an initial rapid increase in a peak at δ 1.98 attributable to the methyl groups of the intermediate. Over a 25-min interval, at 30°, this peak disappears as the peaks for the methyl group (δ 1.93) and the bromomethylene group (δ 3.99) of the product primary allylic bromide gradually increases in area. A parallel observation of the ^{19}F spectrum showed the slow disappearance of a peak, 15.39 ppm upfield from fluorobenzene, attributed to the intermediate, and the appearance of tetrafluorosuccinimide singlet 14.80 ppm upfield of C_6H_5F. Attempts to isolate the intermediate were not successful. The nmr data of Table III can be used, however, to suggest its structure. No evidence for the presence of the vicinal dibromide (**6**, prepared by addition of Br_2) is seen in spectra of the NBTFS reaction mixture. The absence of any bands in the δ 4.5–7.6 region similarly rules out the presence of any appreciable concentrations of the isomeric allylic bromide, **7**.



6



7

Table III. Nuclear Magnetic Resonance Data

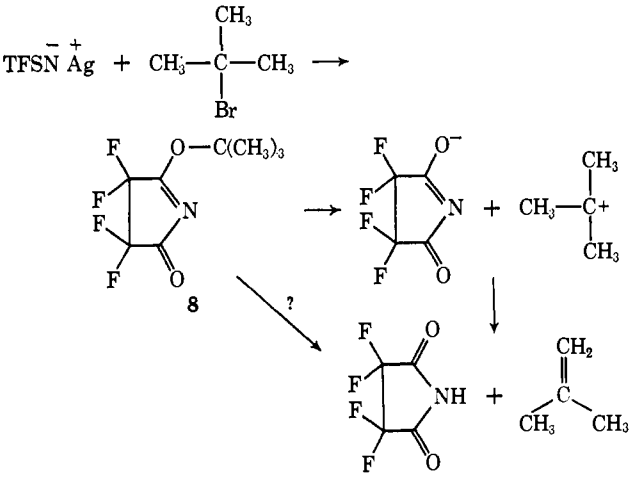
Compound	Solvent	Chemical shifts,[a] δ — Aromatic	Methyl	Other
1g	Benzene		1.56	
	CCl_4	6.72–7.55	1.79	
6	Benzene		1.93	
10 (or **9**)	$CDCl_3$	6.90–7.68	1.98	
	Benzene		1.63	
	CCl_4		1.97	
11	Benzene		1.03	6.48
	CCl_4	6.89–7.89	1.38	6.58
13	CCl_4	6.93–7.51	1.73	6.08
14	CCl_4	7.03–7.86	1.82	5.26

[a] Chemical shifts in parts per million from TMS internal reference.

To distinguish between possible O-alkylated[23] and N-alkylated structures for the intermediate, we compared the nmr spectrum of the intermediate with that of the O-alkylated model compound 2-*t*-butyoxy-5-oxo-3,3,4,4-tetrafluoro-1-pyrroline (**8**). This molecule, which was found to be highly unstable at temperatures greater than −20°, was prepared from the reaction of silver tetrafluorosuccinimide with *t*-butyl bromide at −70° in anhydrous ether. The ^{19}F nmr spectrum of this reaction mixture at −25° showed two triplets (J = 13.3 Hz) 13.80 and 15.24 ppm upfield from fluorobenzene. Warming the reaction mixture to room temperature caused the rapid disappearance of these peaks and the simultaneous appearance of the singlet of tetrafluorosuccinimide. The infrared spectrum of the reaction mixture at −20° (ether solvent) showed a band at 6.33 μ which disappeared as the temperature of the medium was raised. This can reasonably be assigned to the C=N stretching mode.[24]

When **8** was prepared in acetone-d_6 and the reaction medium allowed to warm to room temperature in a sealed tube, the spectrum of isobutylene was observed. Tetrafluorosuccinimide was identified by its infrared spectrum. Scheme B adequately explains these observations.

Scheme B



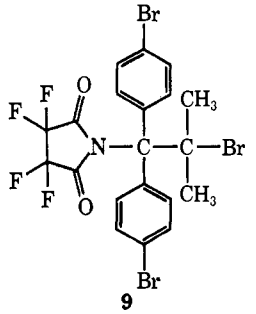
8

The spectrum of the intermediate adduct derived from **1g** and NBTFS is quite different from that of **8**. The ^{19}F nmr spectrum of the adduct in benzene shows a single band 15.39 ppm upfield of fluorobenzene hav-

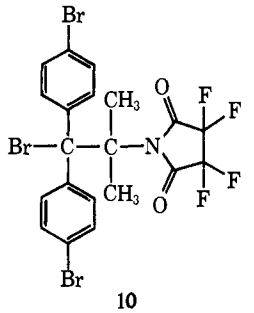
(23) We wish to thank Dr. E. Hedaya for useful discussions of this point.

(24) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1964, p 267.

ing a width at half-height of 15.2 Hz. The considerable breadth of this band may result from the diamagnetic anisotropy of the phenyl rings and possible slow interconversion of rotational isomers. The infrared spectrum of the adduct in CCl_4 at $-20°$ or at room temperature shows no absorption of any significance in the region 6.0–6.5 μ. We therefore conclude that the N-alkylated adducts **9** and **10** are the most probable structures for the intermediate.

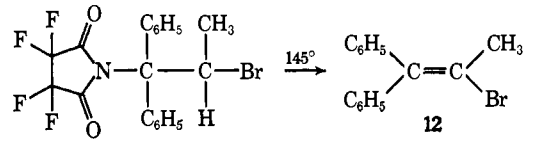


9



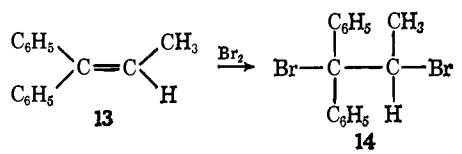
10

The reaction of NBTFS with **1e** gives a stable adduct (**11**) in high yield. The mass spectrum of **11** shows the expected molecular ion peaks at *m/e* 443 and 445 and the most prominent fragmentation pathway involves loss of C_2H_4Br (*m/e* 336 with a metastable ion peak at *m/e* 254) confirming that the addition proceeds in the sense required to give **11** rather than the isomer with reversed position of attachment of the bromine and the succinimidyl fragment. Infrared and ^1H and ^{19}F nmr spectra are also consistent with this structure. Heating a solution of **11** in benzene or carbon tetrachloride at 145° for 8 hr led to quantitative elimination of the perfluorosuccinimide to give **12**.[25]



11 **12**

Analogy might lead us to prefer structure **9** over **10** for the unstable intermediate leading to allylic bromide in the earlier case. In Table III, however, we see a difference of 0.6 ppm in chemical shifts for the methyl groups of **11** and the unstable adduct **9** or **10**. This would seem too large a difference to be attributed to a simple substitution of a methyl group for hydrogen or for the introduction of a *para* substituent into the phenyl ring. (Note the very small difference of 0.1–0.2 ppm in the methyl absorptions of **11** and **14** and of **1g** and **13**.) This suggests that the intermediate leading to allylic bromide from **1g** is really **10**.



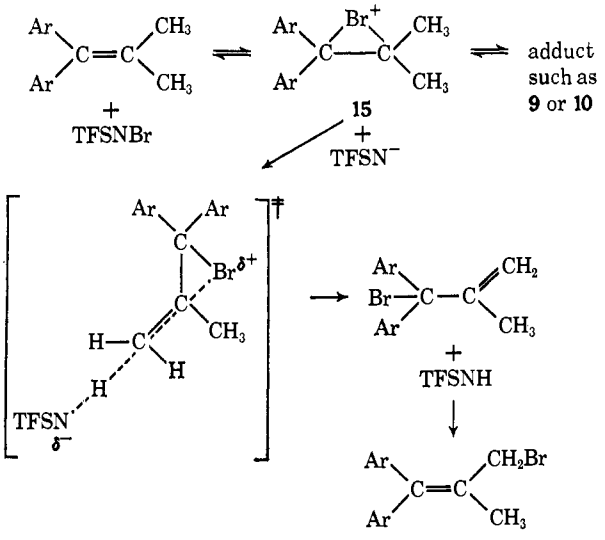
13 **14**

Attempts to observe an intermediate in the reaction of 1,1-diphenyl-2,2-dimethylethylene, **1d**, with NBTFS were less successful. Proton nmr analysis of the reaction mixture immediately after mixing of nearly equivalent amounts of reactants in CCl_4 at room temperature revealed only bands associated with the product allylic bromide and a minor quantity of starting olefin. While fluorine nmr spectroscopy did show a major peak 14.80 ppm upfield of C_6H_5F (tetrafluorosuccinimide) and a minor band assigned to the intermediate, the intensity of the minor band was very low and its disappearance rapid.

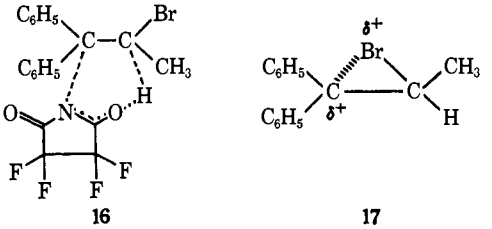
Methyl α-methylcinnamate (**2**) and 1,1-bis(*p*-cyanophenyl)-2,2-dimethylethylene (**1h**) failed to undergo reaction with NBTFS under identical conditions even after 0.5 hr.

The reaction of NBTFS with 1,1-diphenyl-2,2-dimethylethylene, **1d**, gave a 75% yield of adduct in less than 1 min, whereas a comparable degree of reaction of NBTFS with 1,1-bis(*p*-cyanophenyl)-2,2-dimethylethylene, **1h**, is not approached after 2250 min. This allows us to set a lower limit of 2.8 on the value of ρ for the reaction. The large charge separation suggested by this value of ρ is consistent with an ionic pathway for the reaction, involving a transfer of positive bromine from NBTFS, the ionic option of Scheme A.

The considerable difference observed in the reactions of adducts **10** and **11** requires explanation. For the reactions of NBTFS with substituted 1,1-diphenyl-2,2-dimethylethylenes the following mechanism may be written.



The pyrolysis of **11** could occur either through the open diarylmethyl cation or by a molecular mechanism (**16**).



16 **17**

The failure to observe any allylic bromide product from **11** could reflect the smaller amount of positive charge on the carbon α to the methyl in the very unsymmetri-

(25) Where not specified, assignment of the products (*e.g.*, tetrafluorosuccinimide and allylic bromides, etc.) obtained from the reactions of NBTFS with olefins was by comparison of the nmr spectra of the reaction products with those of authentic samples. It is believed that sufficient overlapping data are present in our studies to justify use of this otherwise inferior method for product analyses.

cal bromonium ion **17**.[26] Bromonium ion **15**, more symmetrically substituted than **17**, has more positive charge on the α-carbon and the pathway leading to allylic bromide is of lower energy.

The ionic pathway of Scheme A is important for electron-rich olefins even when radical initiators are present. The addition of inhibitors can make this mechanism predominant in systems which ordinarily undergo radical bromination.

Experimental Section

Materials. The purification of benzene, toluene, *p*-xylene, *p*-*t*-butyltoluene, N-bromosuccinimide, benzoyl peroxide, azobisisobutyronitrile (AIBN), and phthalide are described elsewhere.[9,10] N-Bromotetramethylsuccinimide (NBTMS) and N-bromotetrafluorosuccinimide (NBTFS) were prepared by the method of Pearson.[9,10] Crude triphenylmethylethylene obtained from laboratory stock was recrystallized repeatedly from absolute ethanol to give mp 88.5–90° (lit.[27] mp 89–90°). Crude 1,1-diphenyl-2-methylethylene obtained from laboratory stock was recrystallized repeatedly from absolute ethanol to give mp 51–52.2° (lit.[28] mp 51.5–52°).

Preparation of Olefins 1d, 1g, and 1f. In a typical procedure, powdered benzophenone (50 g, 0.274 mole) was added at room temperature to an ether solution of isopropylmagnesium bromide (0.548 mole) and the reaction mixture refluxed for 3 hr. The resulting mixture was treated with ice-cold aqueous sulfuric acid, extracted with ether, and dried over calcium chloride. Removal of ether left an orange-yellow oil (48.5 g) which upon treatment with a trace of concentrated sulfuric acid and distillation (bp 96° (0.2 mm)) yielded impure **1d** (21.8 g) which was passed through a column of alumina using pentane–ether (3:1) as eluent. Distillation through a 1.5 × 13 cm Vigreux column gave 27% **1d** (15.5 g, 0.074 mole): bp 89° (0.14 mm) (lit.[29] bp 280° (775 mm)); ir (CCl_4) 701, 1445, 1497, 1600 cm^{-1}; nmr (CCl_4) δ 2.42 (s, 6, CH_3), 7.18 (s, 10, aromatic C-*H*).

Crude *p,p'*-dibromodiphenylmethane[30] was oxidized with chromic acid in glacial acetic acid to give *p,p*-dibromobenzophenone, which was treated as above to give **1g**, bp 174° (0.3 mm). Recrystallization six times from pentane–ether (1:1) and once from methanol gave 21% **1g** (11.5 g, 0.031 mole): mp 102–103.5° (lit.[31] mp 96°); ir (CCl_4) 1019, 1078, 1485 cm^{-1}; nmr (CCl_4) δ 1.88, (s, 6, CH_3), 7.24 (d, 4), and 7.55 (d, 4, aromatic C*H*).

Similarly, *p,p'*-dichlorobenzophenone was converted to impure **1f** (bp 143° (0.1 mm)) which was purified by passage through a column of alumina using pentane–ether (1:1) as eluent followed by two recrystallizations from pentane–methanol to give 37% **1f** (18.3 g, 0.073 mole): mp 70–71.5° (lit.[32] mp 71–72°); ir (CCl_4) 1018, 1049, 1487 cm^{-1}.

Preparation of Olefins 1a and 1b. To the Grignard reagent from *p*-bromo-*t*-butylbenzene[33] (75 g, 0.352 mole) and magnesium (8.64 g, 0.355 mole) in ether, ethyl isobutyrate (15.6 g, 0.134 mole) was slowly added to the solution and maintained at reflux for 18 hr. The resulting mixture was treated with aqueous sulfuric acid, extracted with ether, and dried over calcium chloride. Removal of ether left a yellow solid (55.8 g) which was dehydrated with sulfuric acid as above to give 31.3 g of **1b**. Recrystallization, once from absolute ethanol and twice from 1-propanol, gave 58% **1b** (25.0 g, 0.078 mole): mp 119–120°; ir (CCl_4) 830, 912, 1366, 1395, 1503 cm^{-1}; nmr (CCl_4) δ 1.38(5, 9, *t*-butyl), 1.91 (s, 3, CH_3), 7.30 (d, 2, aromatic), 7.55 (d, 2, aromatic). *Anal.* Calcd for $C_{24}H_{32}$: C, 89.93; H, 10.07. Found: C, 90.01; H, 10.01.

A similar procedure converted *p*-bromoanisole to **1a**: mp 68.8–70° (lit.[34] mp 66°); ir (CCl_4) 1045, 1245, 1508, 1606 cm^{-1}; nmr (CCl_4) δ 1.90 (s, 6, C=CH_3), 3.88 (s, 6, OCH_3), 7.00 (d, 2, aromatic), 7.24 (d, 2, aromatic).

1,1-Bis(*p*-cyanophenyl)-2,2-dimethylethylene (1h). The method of Friedman and Schechter[35] was used to convert 1.28 g (3.52 mmoles) of **1g** to **1h** by treatment with cuprous cyanide (1.0 g, 11.2 mmoles) in 10 ml of boiling dimethylformamide for 8 hr. This gave a yellow-brown solid (0.316 g) which was chromatographed on Woelm neutral alumina using ether–pentane (1:1) as eluent and sublimed to give **1h**: mp 105.5–106.5° (lit.[31] mp 90°); ir (CCl_4) 830, 1503, 1605, 2235 cm^{-1}; nmr (CCl_4) δ 1.90 (s, 6, CH_3), 7.28 (d, 2, aromatic), 7.65 (d, 2, aromatic). *Anal.* Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.47. Found: C, 83.34; H, 5.18.

Methyl α-methylcinnamate (2). α-Methylcinnamic acid (5 g, 0.031 mole) was treated with diazomethane (from 10 g of nitrosomethylurea) in ether. Chromatography on alumina gave **2** (4.1 g, 0.023 mole, 75%): mp 40–41.3° (lit.[36] mp 39°).

2-Bromopropane-1,1,1,3,3,3-d_6. Using a procedure related to that of Condon,[37] acetone-d_6 (5 g, 0.078 mole) in sodium-dried ether (10 ml) was added very slowly to a suspension of lithium aluminum hydride (1.48 g, 0.039 mole) in ether (25 ml) at 0°. The reaction mixture was allowed to come to room temperature and maintained at this temperature for 8 hr. The resulting mixture was treated with 50 ml of 3 *M* HCl, extracted with ether, and the ether layer dried over Drierite. The aqueous and ether layers were distilled separately through a 10 × 1 cm column with Heligrid packing. The impure organic distillates obtained from these distillations were combined and redistilled through the same column to yield propan-1,1,1-3,3,3-d_6-2-ol in 68% yield (3.5 g, 0.053 mole), bp 79–80°. To a stirred solution of this in ether, phosphorus tribromide (5.42 g, 0.019 mole) was added at 0–5°, the reaction mixture was allowed to come to room temperature, and was maintained there for 8 hr. Distillation through a 10 × 1 cm Heligrid packed column gave the bromide in 47% yield (3.2 g, 0.025 mole), bp 55–58°.

1,1-Bis(*p*-*t*-butylphenyl)-2,2-dimethyl-d_6-ethylene (1i). *p,p'*-Di-*t*-butylbenzophenone[38] (2.0 g, 6.79 mmoles) was treated with isopropylmagnesium-d_6 bromide (13.4 mmoles) in the usual manner to give a carbinol which was dehydrated in benzene (5 ml) solution boiling for several hours with phosphorus pentoxide (0.5 g, 35.2 mmoles). Chromatography on Woelm neutral alumina using pentane as eluent gave impure **1i** (0.547 g) which was recrystallized from propanol to give 9.8% of the olefin (0.216 g, 0.663 mmole): mp 119–120°; the mass spectrum showed 97% $C_{24}H_{26}D_6$, 3% $C_{24}H_{27}D_5$.

1,1-Diphenyl-2-bromo-2-methylethylene (12). Olefin **1e** (1.12 g, 5.77 mmoles) was dissolved in carbon tetrachloride (0.5 ml) and treated with a slight excess of bromine. The resulting solution was passed through a column of Florisil and the solvent removed to give **1e** (0.885 g, 3.24 mmoles): nmr (CCl_4) δ 2.43 (s, 3, CH_3), 7.21 (s, 5, aromatic).

N-(1,1-Diphenyl-2-bromopropyl)tetrafluorosuccinimide (11). Olefin **1e** (0.374 g, 1.93 mmoles) was dissolved in benzene (5 ml), cooled to 5°, and treated, with stirring, with an ice-cold solution of NBTFS dissolved in 5 ml of benzene. The reaction was exothermic. After 0.5 hr at room temperature the solvent was removed under vacuum to give **11** (0.820 g, 1.16 mmoles): mp 120–131°; ir (CCl_4) 1073, 1175, 1301, 1760 cm^{-1}; nmr (CCl_4) δ 1.35 (d, 3, J = 7 Hz, CH_3), 6.61 (q, 1, J = 7, methine C-*H*), 7.2–7.7 (m, 5, aromatic); ^{19}F nmr (C_6H_6), singlet 15.59 ppm upfield from C_6H_5F. *Anal.* Calcd for $C_{19}H_{14}F_4NO_2Br$: C, 51.36; H, 3.17; Br, 18.00. Found: C, 51.64; H, 3.05; Br, 17.30.

A sample of this compound (0.027 g, 0.083 mmole) in 0.4 ml of carbon tetrachloride was sealed in an nmr tube and heated at 145° for 8 hr: ^{19}F nmr, singlet 14.80 ppm upfield of C_6H_5F which increased in intensity upon addition of tetrafluorosuccinimide ^1H nmr identical with that of **12**.

Reaction of NBTFS with 1g. Olefin **1g** (0.059 g, 0.161 mmole) was dissolved in an nmr tube in 0.3 ml of benzene. A solution of N-bromotetrafluorosuccinimide (0.037 g, 0.149 mmole) in 0.3 ml of benzene was rapidly added in the dark at room temperature, the contents of the tube were mixed, and the nmr spectrum was taken immediately. The yield of allylic bromide was established in the usual manner using phthalide as an internal standard.

Bromination by N-Bromoimides. Competitive brominations at 80° using N-bromoimides were carried out in purified benzene using AIBN or benzoyl peroxide as initiator. The Y-shaped reaction

(26) K. Yates and W. V. Wright, *Can. J. Chem.*, **45**, 166 (1967).
(27) M. J. Levy, *Bull. Soc. Chim. France*, 120 (1921).
(28) "Handbook of Chemistry and Physics," 43rd ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 1182.
(29) A. Brodhog and C. R. Hauser, *J. Am. Chem. Soc.*, 77, 3024 (1955).
(30) N. E. Goldthwaite, *Am. Chem. J.*, **30**, 457 (1903).
(31) J. N. Ashley, J. F. Grove, and T. Henshall, *J. Chem. Soc.*, 261 (1948).
(32) W. J. Hickinbottom and G. E. M. Moussa, *ibid.*, 4195 (1957).
(33) E. Berliner and F. J. Bondhus, *J. Am. Chem. Soc.*, **68**, 2355 (1946).
(34) N. D. Xuong and N. P. Buu-Hoi, *J. Chem. Soc.*, 3741 (1952).
(35) L. Friedman and H. Schechter, *J. Org. Chem.*, **25**, 877 (1960).
(36) L. Edeleano, *Ber.*, **20**, 616 (1887).
(37) F. E. Condon, *J. Am. Chem. Soc.*, **73**, 4675 (1951).
(38) B. W. Larner and A. T. Peters, *J. Chem. Soc.*, 680 (1952).

vessel consisted of two bulbs sealed to one another and to a third smaller piece of tubing having a male joint appropriate for attachment to a vacuum line. Two or three olefinic or benzylic substrates, plus the initiator or inhibitor, were accurately weighed directly into one of the bulbs of the reaction vessel. The N-bromoimide was weighed into the other bulb and 5 ml of benzene added to each bulb. The reaction mixture was degassed three times at 0.05–0.1 mm, sealed, immersed in an oil bath at 80°, allowed to reach thermal equilibrium (3–4 min), and the contents of the bulbs were rapidly mixed. Upon mixing, the solution of the N-bromoimide was always added, with swirling, to that of the substrates.

Competitive NBS brominations at 25° were carried out in purified benzene using benzoyl peroxide as initiator. The reaction vessel used was a cylinder 1 ft long and 3 in. in diameter, sealed at one end with a vacuum stopcock and male joint at the other. All components of the reaction mixture were weighed, dissolved in benzene, and transferred quantitatively to the reaction vessel. The reaction medium was degassed three times, sealed from the atmosphere by a stopcock, immersed in a water bath at 25°, and irradiated with magnetic stirring for 4 hr, using a 270-W G.E. sunlamp.

Glassware used in the competitive rate studies was treated with aqua regia for 1 hr at 100°, rinsed with water, treated with concentrated ammonium hydroxide, rinsed repeatedly with water, and dried at 150–200°.

Bromination by Molecular Bromine. Brominations employing molecular bromine were carried out at 25 ± 2° in benzene. The reaction vessel was a 1000-ml round-bottomed flask modified such that the tips of four capillary tubes could be immersed into the reaction mixture nearly to the base of the flask. The weighed reaction substrates were dissolved in 250 ml of benzene in the reaction vessel and immersed in a water bath at 40° with magnetic stirring. A steadily increasing flow of nitrogen (Matheson prepurified) was introduced into the solution *via* three capillary tubes. Such a procedure served both to slowly lower the temperature and to deoxygenate the reaction medium. A G.E. sunlamp was used to irradiate the solution. When the desired temperature (25°) was attained, the nitrogen flow was rerouted through a by-pass allowing a weighed quantity of dilute gaseous bromine to be carried into the reaction medium. After an induction period of a few seconds (usually 2–5 sec), the light red-brown color of bromine in the solution was no longer noticed and the presence of hydrogen bromide in the exit gases was immediately evident. Since the reaction time (60–90 sec) was so short more extensive efforts at temperature control were considered unnecessary. A 270-W G.E. sunlamp provided the ultraviolet radiation.

Analysis of the Product Mixtures. The addition of weighed quantities of an internal standard (phthalide) to the product mixture allowed ready analysis of the reaction products by nmr spectroscopy. In general, five integrals were run for every sample and deviations seldom exceeded ±2%. Concentration of the product mixtures, where necessary, was carried out using a rotary evaporator at 40° (80–120 mm).

The Quantitative Determination of 1,1-Bis(*p*-*t*-butylphenyl)-2,2-dimethyl-d_6-ethylene (11) in Product Mixtures. In runs where the deuterated olefin **1i** was used as a competitive substrate, mass spectrometry was used to determine the final quantity of this substrate present in the reaction medium after reaction. The undeuterated analog **1b** was weighed into the reaction mixture immediately after the reaction was complete to serve as an internal standard. Comparison of the heights of the peaks at *m/e* 320 and 326 allowed accurate calculation of the quantity of **1i** remaining after reaction. In those runs where the standard served also as a competitive reactant, nmr analysis was employed in determining the quantity of this olefin remaining after reaction.

Work-up consisted of careful removal of solvent, passage of the nonvolatile remaining oil in pentane through Florisil and/or alumina to remove the product bromides, and mass spectrometric analysis of the recovered mixture of olefins. Control analyses of mixtures of known quantities of **1i** and **1b** gave agreement between measured and known ratios within ±2%.

Acknowledgment. This work was supported in part by a grant from the U. S. Public Health Service, GM-12296.

Nuclear Magnetic Resonance Evidence for the Pathways of Pseudorotation in Alkyloxyphosphoranes

David Gorenstein[1] and F. H. Westheimer

Contribution from the James Bryant Conant Laboratory, Harvard University, Cambridge, Massachusetts 02138. *Received May 15, 1969*

Abstract: In previous communications[2,3] we showed that alkyloxyphosphoranes containing five-membered rings undergo pseudorotation about the pentacovalent phosphorus atom, subject to the constraints imposed by considerations of ring strain and of the preference for placing alkyl groups in equatorial positions. A process of ring opening and reclosure, which can equilibrate some of the groups in a phosphorane, was also found, but only at high temperatures, and is clearly distinguished from pseudorotation. A number of new alkyloxyphosphoranes have now been synthesized; a study of their nmr spectra shows that, at least in most instances, pseudorotation occurs by surmounting the energy barrier required to place an alkyl group in an apical position. In addition, a second and different process occurs in one phosphorane to equilibrate groups that are not mixed by the usual pathway for pseudorotation. Possibly the substantially higher barrier that is associated with this second process is that required to place a five-membered ring in diequatorial positions in a phosphorane. Additional experiments confirm and make more secure the distinction between ring opening and pseudorotation in cyclic alkyloxyphosphoranes.

The chemistry of cyclic esters of phosphoric acid and of related esters of phosphonic and phosphinic acids has led to the concept[4–9] that the hydrolysis of these esters may, and on occasion must be accompanied

(1) National Institutes of Health Predoctoral Fellow, 1967–1969. Address Correspondence to author at: Chemistry Department, University of Illinois, Chicago Circle, Chicago, Ill.

(2) D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **89**, 2762 (1967).

(3) D. Gorenstein and F. H. Westheimer, *Proc. Nat. Acad. Sci. U. S.*, **58**, 1747 (1967).

(4) E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3431 (1966); *ibid.*, **88**, 3432 (1966).

(5) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70, (1968).

(6) R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 91, 4143 (1969).

(7) R. Kluger, F. Covitz, E. A. Dennis, L. D. Williams, and F. H. Westheimer, *ibid.*, **91**, 6066 (1969).

(8) D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967).

(9) W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968).