Polar Radicals. V. The Free-Radical Bromination of Cyclohexyl Bromide and 1-Bromobutane with *N*-Bromosuccinimide and Molecular Bromine[1]

Dennis D. Tanner,* Melvin W. Mosher,[2] N. C. Das,[3] and E. V. Blackburn[4]

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received December 22, 1970*

Abstract: The free-radical brominations of cyclohexyl bromide and 1-bromobutane with *N*-bromosuccinimide (NBS) have been investigated. These brominations can be carried out under specific conditions with a minimum of interference from the reversible reaction of the alkyl radicals and the hydrogen bromide produced. These conditions, homogeneous acetonitrile solutions of NBS and bromoalkane (1:4) containing 3% AIBN as initiator at 40°, in the dark, allowed an estimate of the true kinetically determined distribution of radicals produced in the bromination of these bromoalkanes. The product distributions approaching those predicted from normal polar effects were observed and no evidence of anchimeric assistance by the neighboring bromine atom could be found in these systems.

We have recently demonstrated the absence of anchimeric assistance in the photobromination of 1-bromobutane with molecular bromine.[5] The dominance of the 1,2-dibromide in the products, which was previously believed to be due to the acceleration of the abstraction of the β-hydrogen by the neighboring bromine,[6-9] was proposed to be due to the reversible nature of the abstraction reaction with the hydrogen bromide produced in the reaction (eq 1).[5]

$$C_4H_9Br + Br\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_8Br\cdot + HBr \qquad (1)$$

Transfer reactions subsequent to the abstraction lead to the production of 1,2-dibromide, almost to the exclusion of the other dibrominated products, once an appreciable amount of hydrogen bromide is produced. In the initial stages of the reaction the distribution of products reflected the normal distribution of products predicted[5] for the bromination of a negatively substituted butane (see reaction 1, Table I). The product distribution was found to vary with percentage reaction (*i.e.*, hydrogen bromide concentration) until, at the completion of reaction, ~90% of the dibrominated material was 1,2-dibromobutane (see reaction 2, Table I).

Table I. Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of 1-Bromobutane with Molecular Bromine[a]

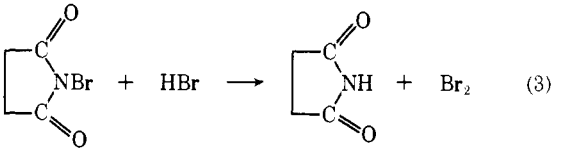
	Isomer distribution				
Reaction	1,4 C	1,3 C	1,2 C	1,1 C—Br	Reaction, %
1	...	1.00	0.53	0.52	2
2	...	1.00	7.30	Trace	95

[a] Reference 5.

An attempt was made to eliminate the effect of hydrogen bromide on the product distribution by carrying out the 1-bromobutane brominations with *N*-bromosuccinimide (NBS). By utilizing the well-established chain mechanism for aliphatic bromination by NBS[10-12] (Scheme I), it was anticipated that the hydrogen bromide concentrations could be kept low enough to limit the reverse reaction.

Scheme I

$$RH + Br\cdot \longrightarrow R\cdot + HBr \qquad (2)$$



$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (4)$$

This attempt was unsuccessful when the reactions were carried out either by the photolysis of heterogeneous mixtures of the substrate and NBS or by irradiation of homogeneous acetonitrile solutions of the reactants.[5] We have since established satisfactory experimental conditions for a study of the brominations of alkanes and substituted alkanes in the absence of hydrogen bromide. The report of the results of the NBS bromination studies, using 1-bromobutane and cyclohexyl bromide as models, is the purpose of this publication.

Results and Discussion

Photobromination of cyclohexyl bromide with molecular bromine has been reported to give six products.[8] Five of the six compounds were shown to be trans 1,2- and cis and trans 1,3- and 1,4-dibromides by glpc comparison with authentic samples. The remaining compound was not positively identified but was thought to be either *cis*-1,2-dibromocyclohexane or 1,1-dibromocyclohexane. We have repeated the bromination of

(1) Part IV: D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *J. Amer. Chem. Soc.*, **93**, 4802 (1971).
(2) University of Alberta, Postdoctoral Fellow, 1967–1969.
(3) University of Alberta, Postdoctoral Fellow, 1968–1969.
(4) University of Alberta, Postdoctoral Fellow, 1969–1971.
(5) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 7398 (1969).
(6) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).
(7) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).
(8) W. Thaler, *ibid.*, **85**, 2607 (1963).
(9) J. G. Traynham and W. G. Hines, *ibid.*, **90**, 5208 (1968).
(10) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963), and references cited therein.
(11) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963).
(12) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

Table II. Chemical Shifts and Peak Widths of C*H*Br Absorptions

Peak no.	Peak position in cps from TMS		Peak width in cps[b]		Compd
	Lit. value[a]	Expt determined	Lit. value[a]	Expt determined	
2	268	268	8–9	8.5	*trans*-1,2-Dibromocyclohexane
3	270	270	13	13.0	*trans*-1,3-Dibromocyclohexane
4	255	255	13–14	13.5	*cis*-1,4-Dibromocyclohexane
5	228	228	25	25.0	*cis*-1,3-Dibromocyclohexane
6	257	257	13–15	14.0	*trans*-1,4-Dibromocyclohexane

[a] Reference 13. [b] Measured at half the peak height.

Table III. Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of Bromocyclohexane with NBS

Reaction	Time, hr	% reaction[b]	Peak ratios[a]					
			1,1	Trans 1,2	Trans 1,3	Cis 1,4	Cis 1,3	Trans 1,4
1	10 (min)	2	0.3	0.25	1.0	0.4	0.4	0.4
2	30 (min)	5	0.4	0.3	1.0	0.4	0.5	0.4
3	1	10	0.6	0.4	1.0	0.4	0.6	0.5
4	3	20	0.7	0.5	1.0	0.6	0.7	0.7
5	6	40	0.7	1.2	1.0	0.6	0.6	0.5
6	9	60	0.6	1.7	1.0	0.8	0.8	0.8
7	12	80	0.6	2.0	1.0	0.8	0.8	0.8
8	24	100	0.5	2.0	1.0	0.7	0.7	0.7

[a] Fractional ratios relative to the amount of *trans*-1,3-dibromocyclohexane. [b] The value reported represents a material balance for the products determined.

bromocyclohexane under the conditions reported by Thaler.[8] Glpc analysis indicated the formation of six products in the ratio 1.0:37.8:3.5:3.8:2.6:2.0. The compounds were isolated by preparative glpc. Five of the compounds had the structures reported by Thaler.[8] Their ^{1}H nmr spectra were determined and the peak positions and width of the C*H*Br absorptions were determined. These values were in agreement with the literature values[13] for the compound assignments and are shown in Table II.

We have now shown that the sixth compound is 1,1-dibromocyclohexane by comparison (glpc retention time, mass spectra, and ^{1}H nmr) with an authentic sample of 1,1-dibromocyclohexane prepared by the method of Kwestroo, Meijer, and Havinga.[14]

We have recently reported[5] the variation of product distribution with per cent conversion in the photobromination of 1-bromobutane with molecular bromine. The experimental observations clearly ruled out participation by a neighboring bromine atom in the rate-determining abstraction step in this reaction.

We have therefore reinvestigated the photobromination of cyclohexyl bromide with molecular bromine to see if a similar phenomenon is operative in this system. Using essentially the same reaction conditions as were reported by Thaler in his study of the bromination of cyclohexyl bromide[8] we irradiated a mixture of molecular bromine (1 mol) and cyclohexyl bromide (4 mol) in a sealed degassed Pyrex ampoule at 40° with an incandescent lamp until the reaction mixture was colorless (~24 hr). The reaction products were analyzed (glpc) by the reported procedure,[8] and the isomer distribution of dibrominated cyclohexanes was found to be in agreement with that reported by Thaler.[8] However, when a series of these reactions was carried out and the photolysis stopped before the bromination was complete, analysis of the reaction mixtures did not show a variation of the isomer distribution with the percentage reaction. Thus, peak 2 (*trans*-1,2-dibromocyclohexane) was about 95% of the total product even at 1.3% conversion.

This predominance of the trans 1,2-dibromide might have been due to a dark bromination of cyclohexyl bromide analogous to the bromination of *tert*-butyl bromide.[15] However, no reaction was observed when a sealed Pyrex tube, containing the reaction mixture, was left in the dark for 48 hr. Similarly, a degassed saturated solution of hydrogen bromide in cyclohexyl bromide did not react.

The bromination of cyclohexyl bromide was repeated using a degassed homogeneous solution of NBS in acetonitrile containing bromobenzene as an internal standard. The tubes were irradiated in a "merry-go-round" apparatus at 40° for varying lengths of time, using 2 × 200 W tungsten bulbs. The tubes were opened and titrated against standard sodium thiosulfate solution. Methylene chloride was added to extract the dibromides and bromobenzene. The methylene chloride was removed by distillation at room temperature. The concentrated solutions were analyzed on a 10 ft × $^1/_8$ in. 10% diethylene glycol succinate column and the results are given in Table III.

From these results it can be seen that even at 100% reaction, the *trans*-1,2-dibromobutane is only 35.7% of the total product. The exchange reaction of the bromocyclohexyl radicals with HBr has been considerably more suppressed by the use of NBS than in the case of the 1-bromobutane brominations with NBS where 1,2-dibromobutane was the major product (>84%) at 100% reaction.[5] The results reported in the present article show that the formation of 1,2-dibromocyclohexane as the major reaction product (>94%),[8] from the bromination of cyclohexyl bromide with molecular bromine, cannot be taken as evidence for anchimeric assistance by neighboring bromine since in the NBS bromination of cyclohexyl bromide (also a

(13) H. M. van Dort and Th. J. Sekuur, *Tetrahedron Lett.*, 1301 (1963).

(14) W. Kwestroo, F. A. Meijer, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 73, 717 (1954).

(15) G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 77, 4025 (1955).

Table IV. Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of Cyclohexyl Bromide with NBS Using AIBN as Chain Initiator

Reaction	Time, hr	% reaction	Peak ratios 1,1	Trans 1,2	Trans 1,3	Cis 1,4	Cis 1,3	Trans 1,4
1	6	2	0.51	0.22	1.0	0.72	0.71	0.50
2	19	8	0.56	0.20	1.0	0.80	0.71	0.52
3	93	36	0.55	0.55	1.0	0.77	0.69	0.55
4	192	50	0.47	0.68	1.0	0.75	0.72	0.55
5	382	64	0.50	0.97	1.0	0.60	0.71	0.60
6	554	84	0.55	1.21	1.0	0.62	0.71	0.54
7	888	92	0.46	1.39	1.0	0.59	0.70	0.53
8	1464	96	0.46	1.57	1.0	0.62	0.70	0.60

result of bromine radical abstraction), the product isomer distribution varied with per cent reaction, and is therefore not the result of kinetic control.

Total suppression of any HBr buildup in the reaction tubes might be expected to permit the final product distribution, in the bromination of bromoalkanes, to reflect the distribution of the initial kinetically formed radicals. The conditions necessary to permit such a reaction would involve the production of very low concentrations of molecular bromine, thus producing very low concentrations of HBr which could be removed from the reaction by NBS. We now report the results of such an investigation using cyclohexyl bromide and 1-bromobutane as substrates.

The reaction mixtures consisted of 1:4 molar ratios of NBS to the purified alkyl halide in purified acetonitrile as solvent containing 3% azobisisobutyronitrile (AIBN) as radical initiator. Pyrex ampoules containing the reaction mixtures were degassed in the dark, immersed in a thermostated oil bath at 40°, and maintained in the dark. The tubes were removed after varying lengths of time and the amount of unreacted NBS was determined by titration against standard sodium thiosulfate solution. The product distribution was determined by glpc on a 10 ft × 1/8 in. diethylene glycol succinate (DEGS) column after the brominating agent had been removed. The product distributions obtained with cyclohexyl bromide as substrate are shown in Table IV and the results with 1-bromobutane in Table V.

Table V. Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of 1-Bromobutane with NBS Using AIBN as Chain Initiator

Reaction	Time, hr	Reaction, %	C———C	C———C	C———C—Br
1	13	9	...	1.00	0.30	0.27
2	36	15	...	1.00	0.65	0.31
3	40	24	...	1.00	0.43	0.28
4	156	37	...	1.00	0.84	0.28
5	253	51	Trace	1.00	1.36	0.34
6	600	55	0.08	1.00	1.25	0.38
7	1152	57	0.08	1.00	1.37	0.33

The results in Table IV indicate that HBr reversal is far less important when radical rather than when light initiation is utilized in these brominations with NBS. The more rapid photoinitiated reaction turned a dark bromine color during the initial stages of the reaction and the bromination proceeded, presumably, at least in part, utilizing this molecular bromine.

The relative reactivity per hydrogen has been reported for the photochlorination of cyclohexyl bromide and of cyclohexyl chloride.[16a,b] These results are compared with the observed relative rate data obtained in the bromination reactions of cyclohexyl bromide (Table VI).

Table VI. The Relative Reactivities per Hydrogen in the Initiated Halogenation of $C_6H_{11}X$

X	Reagent	Rel reactivities/hydrogen atom[a] α	β	γ	δ
Cl[b]	Cl_2	0.36	0.44	0.79	1.0
Br[b]	Cl_2	0.40	0.20	0.91	1.0
Br	Molecular Br_2	0.34	3.26	0.52	1.0
Br	NBS–AIBN at 96% reaction	0.75	0.64	0.70	1.0
Br	NBS–AIBN at 2% reaction	0.84	0.09	0.70	1.0

[a] Values were calculated for β, γ, and δ positions using the combined yields of cis and trans dibromides. [b] Reference 16a.

Table VI shows the similarity between the relative reactivities found in the bromination of cyclohexyl bromide with homogeneous solutions of NBS, using AIBN as initiator, and those observed in the photochlorination of bromo- and chlorocyclohexane. Thus, the product distribution at 96% reaction indicates that the relative reactivity per hydrogen at the β position is no longer greater than the relative reactivity per hydrogen at the γ position (as is the case in the brominations with molecular bromine), and so more nearly reflects the distribution of the initial kinetically formed radicals.

The rate of the AIBN-initiated bromination of 1-bromobutane became very slow and was stopped at 57% conversion (Table V). The 1,2-dibromobutane did not become the major product until 40% reaction and this result can be compared with the photoinitiated bromination of 1-bromobutane with heterogeneous mixtures of NBS, when the 1,2-dibromide was the major product at all stages of the reaction[5] or when the reaction was carried out in homogeneous solution where the 1,2-dibromide was the major product after 23% conversion.

The presence of an excess of NBS would be expected to more completely prevent any buildup in HBr concentration as the reaction proceeds. We have established a method which suppresses involvement of HBr

(16) (a) G. A. Russell, A. Ito, and R. Konaka, *J. Amer. Chem. Soc.*, 85, 2988 (1963). (b) Russell has rationalized the cis to trans ratios observed in the photochlorinations of cyclohexyl chloride[16a] and a similar discussion of the bromination reactions of cyclohexyl bromide can be made.

in the bromination reactions to a considerable degree and are in the process of investigating other systems using a threefold excess of NBS in an attempt to eliminate HBr involvement as completely as possible.

1-Bromobutane undergoes a radiation-induced isomerization to 2-bromobutane with hydrogen bromide acting as a chain-transfer agent.[17] Similarly, radiolysis or photolysis of isobutyl bromide results in isomerization to *tert*-butyl bromide.[18] The data presented in our previous publication[5] for the yield of 1,1-, 1,2-, 1,3-, and 1,4-dibromobutanes during the course of the photobromination of 1-bromobutane led us to suspect that the 1,1- and 1,3-dibromobutanes might be rearranging under the reaction conditions. The brominations were repeated in the presence of added dibromide, and the composition of the final mixture determined by glpc using Freon-113 as an internal standard. In both cases rearrangement of the dibromide, if present, was too small to be experimentally significant. Thus, the high yield of 1,2-dibromobutane from the photobromination of 1-bromobutane is not a result of a hydrogen bromide catalyzed free-radical rearrangement.

We have conclusively eliminated the possibility of anchimeric assistance by the neighboring bromine atom during β-hydrogen abstraction in these two systems. An attractive alternative explanation for the observed product distribution was suggested in terms of the acid-assisted elimination of a bromine atom from the β-bromoalkyl radical to form an olefin and the subsequent addition of molecular bromine to form the 1,2-disubstituted dibromide.[5] We have recently found, using bromine-81 as the brominating agent, that there is no isotopic enrichment of the dibrominated products formed under the reaction conditions used in the bromination of 1-bromobutane[19] or 1-bromo-2-methylbutane,[1] presumably ruling out the formation of "free" olefinic intermediates.

Since we have eliminated the possibility of anchimeric assistance by neighboring bromine in the radical abstraction of a secondary β-hydrogen, and since the final product distribution seems to be influenced by the concentration of hydrogen bromide in the solution, an alternative explanation for the formation of 1,2-dibrominated product seems in order. If transfer with hydrogen bromide is important in the determination of the products, then kinetically there would be a competitive transfer reaction of the radical with hydrogen bromide and with molecular bromine. Since

$$\mathrm{Br}\cdot + \mathrm{RBr} \xleftarrow{\mathrm{Br_2}} \mathrm{R}\cdot \xrightleftharpoons{\mathrm{HBr}} \mathrm{RH} + \mathrm{Br}\cdot$$

in the bromination of substituted alkanes the reactions were much slower in the presence of hydrogen bromide,[5] the reversible reaction must be competitive with transfer with molecular bromine.

The following inequality in transfer rates would lead to the production of 1,2-dibrominated products at high hydrogen bromide concentration, where rate^{β} is the rate of transfer of the β radical with the indicated transfer agent and (rate^{i}) is the rate of transfer of all the other radicals.

$$\frac{\mathrm{rate}^{\beta}_{\mathrm{Br_2}}}{\mathrm{rate}^{\beta}_{\mathrm{HBr}}} > \frac{\mathrm{rate}^{i}_{\mathrm{Br_2}}}{\mathrm{rate}^{i}_{\mathrm{HBr}}}$$

The cause of the inequality may well be the stabilization of the β-bromoalkyl radical by bridging after abstraction, or by a polar destabilization of the β radical to HBr transfer, but at this time no clear choice of the controlling effects can be made, and further work on these systems is now in progress.

Experimental Section

Materials. All chemicals were commercially available. Purification of 1-bromobutane and cyclohexyl bromide was accomplished by washing with concentrated sulfuric acid followed by fractional distillation. Acetonitrile was distilled from phosphorus pentoxide and stored over activated molecular sieve no. 3A. Bromine was distilled *in vacuo* and *N*-bromosuccinimide (97% by titration) was used without further purification. The purity of the volatile substrates and solvent was checked by glpc.

Bromination of Cyclohexyl Bromide with Molecular Bromine. The reaction mixture consisted of a 1:4 molar ratio of bromine to the neat alkyl halide. The solutions were degassed by the freeze–thaw method and irradiated in sealed Pyrex ampoules with two 200-W incandescent lamps at 40°. The ampoules were removed after various lengths of time, the solutions were titrated against standard sodium thiosulfate, and the reactions were analyzed on a 10 ft × 1/8 in. DEGS glpc column. No change was observed in product distribution with percentage reaction.

The six dibromides, present in the ratio 1.0:37.8:3.5:3.8:2.6:2.0, were isolated by preparative glpc using 10 ft × 1/4 in. DEGS glpc column and their ^{1}H nmr spectra were determined on a Varian HA-100 instrument. Peaks 2–6 were shown to be *trans*-1,2-dibromocyclohexane, *trans*-1,3-dibromocyclohexane, *cis*-1,4-dibromocyclohexane, *cis*-1,3-dibromocyclohexane, and *trans*-1,4-dibromocyclohexane by comparison of their nmr spectra with those of previously reported spectra.[13] Peak 1 was identified as corresponding to 1,1-dibromocyclohexane by comparison of its glpc retention times and ^{1}H nmr spectra with those of an authentic sample.[14]

Reaction of Cyclohexyl Bromide and Molecular Bromine in the Dark. The reaction mixture consisted of a 1:4 molar ratio of bromine to neat cyclohexyl bromide. The solutions were degassed in sealed Pyrex ampoules which were wrapped in silver foil and placed in a thermostated bath in the dark at 40°. The unreacted bromine was treated with potassium iodide and potassium thiosulfate and the organic substrate was analyzed by glpc. No detectable amount of dibromides was formed after 48 hr.

The Treatment of Cyclohexyl Bromide with Hydrogen Bromide in the Dark. Cyclohexyl bromide was saturated with anhydrous hydrogen bromide and the amount of hydrogen bromide was determined by titration against standard sodium hydroxide solution. The saturated cyclohexyl bromide was degassed and sealed in a Pyrex ampoule and placed in a thermostated bath in the dark at 40°. The acid content had not changed after 7 days. Glpc analysis indicated the absence of any reaction.

Bromination of Cyclohexyl Bromide with NBS. NBS (1.575 g; 0.00875 mol), purified cyclohexyl bromide (5.740 g; 0.0353 mol), and bromobenzene (1.600 g; 0.00125 mol) were dissolved in purified acetonitrile (14 ml) and 1 ml of the solution was put into each ampoule which was then degassed and sealed. The solutions were irradiated at 40° in a merry-go-round apparatus using two 200-W incandescent lamps. The tubes were removed after varying lengths of time. The tubes were cooled in liquid air and then broken open. The reaction mixtures were treated with potassium iodide and titrated against standard sodium thiosulfate to determine the per cent reaction. The amount of reaction was further verified by glpc analysis using the internal standards; these results agreed to ±1%. The solution was extracted with methylene chloride which was then removed by reduced pressure distillation at room temperature and the mixture was analyzed by glpc using a 10 ft × 1/4 in. 5% DEGS glpc column. The results are shown in Table III. It is important to note that the unreacted NBS *must be destroyed* before glpc analysis as erroneous results can be obtained due to bromination in the injector port of the glpc instrument.

The Azobisisobutyronitrile-Initiated Bromination of Cyclohexyl Bromide with NBS. The reaction mixtures consisted of NBS (0.00986 mol), cyclohexyl bromide (0.0340 mol), and acetonitrile (14 ml) containing 3% AIBN. Aliquots of these solutions were

(17) D. H. Martin and F. Williams, *J. Amer. Chem. Soc.*, **92**, 769 (1970).
(18) D. K. Bakale and H. A. Gillis, *J. Phys. Chem.*, **74**, 2074 (1970).
(19) D. D. Tanner, M. W. Mosher, N. J. Bunce, E. V. Blackburn, and H. Yabuuchi, unpublished results from this laboratory.

placed in Pyrex ampoules and degassed by the freeze–thaw method. The tubes, which were always protected from light, were immersed in a thermostated oil bath at 40°. The individual reactions were removed at the desired intervals and analyzed as above. The results are shown in Table IV.

The Azobisisobutyronitrile-Initiated Bromination of 1-Bromobutane with NBS. The reaction mixtures consisted of NBS (2.143 g; 0.0120 mol), 1-bromobutane (6.861 g; 0.0508 mol), and acetonitrile (20 ml) containing 3% AIBN. The solutions were degassed by the freeze–thaw method in the dark, wrapped in silver foil. The tubes were immersed in a thermostated bath at 40° and then removed after varying lengths of time and analyzed as above. The results are shown in Table II.

Photobromination of 1-Bromobutane in the Presence of Added 1,1-Dibromobutane. Solutions of 1-bromobutane (0.0067 mol), bromine (0.0016 mol), 1,1-dibromobutane (0.00099 mol), and Freon-113 (0.0010 mol) were degassed in a sealed Pyrex ampoule and irradiated by two 200-W bulbs until colorless. Glpc analysis was carried out using a 10 ft × 1/4 in. 5% DEGS column and the product distribution was determined using a calibration curve. The product composition was 1,1-dibromobutane (0.0011 mol), 1,2-dibromobutane (0.0016 mol), 1,3-dibromobutane (0.00020 mol), and 1-bromobutane (0.0050 mol).

Photobromination of 1-Bromobutane in the Presence of Added 1,3-Dibromobutane. Solutions of 1-bromobutane (0.0208 mol), bromine (0.0062 mol), 1,3-dibromobutane (0.00366 mol), and Freon-113 (0.00383 mol) were degassed in a Pyrex ampoule and irradiated until colorless and the product distribution was determined using a calibration curve. The product composition was 1-bromobutane (0.0151 mol), 1,2-dibromobutane (0.00557 mol), and 1,3-dibromobutane (0.00433 mol).

Acknowledgment. The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work.

Tetraazanaphthalene Radical Anions

R. Danieli,[1a] L. Lunazzi,*[1b] and G. Placucci[1b]

Contribution from the Laboratorio dei Composti del Carbonio Contenenti Eteroatomi, C. N. R., Ozzano Emilia, Italy, and the Institute of Organic and Industrial Chemistry, University of Bologna, 40136 Bologna, Italy. *Received January 28, 1971*

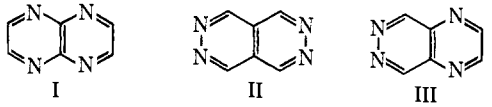
Abstract: The esr spectra of three tetraazanaphthalene radical anions are reported. Comparison is made among assignments obtained by MO calculations, empirical rules, and experimental methods. The effect of the choice of the k_{NN} resonance integral upon the calculated spin densities is discussed.

The esr spectra of azanaphthalene radical anions have been investigated by many authors with the purpose of assigning proton and nitrogen hyperfine splittings both experimentally and theoretically.[2-6] In the molecular orbital framework, Coulomb (h_N) and resonance (k_{CN}) integrals for the nitrogen atom were thus quite well defined[2a,4-8] and attempts were undertaken to make assignments by using more sophisticated calculations. In some cases they were found, however, to disagree with the results of the standard McLachlan spin densities, but experimental assignment confirmed the correctness of the McLachlan method.[5,6]

Empirical rules were also proposed as a possible alternative in assigning hyperfine splittings[9,10] and they gave satisfactory results when applied to diazanaphthalene radicals.[4,6] In order to verify whether these rules may be extended to systems with four nitrogen atoms in different ring positions as well as to study the effects of the molecular orbital parameters on the calculated spin densities, three isomeric tetraazanaphthalene radicals were investigated.

Results and Discussion

The radical anions of three among the possible tetraazanaphthalene isomers, namely the 1,4,5,8-(I), the 2,3,6,7- (II), and the 1,4,6,7- (III) tetraazanaphthalenes,



I II III

were obtained and their esr spectra examined. In the experimental conditions employed, the free anions are believed to be obtained since no evidence was detected of splittings due to the counterion and, furthermore, the spectrum of radical 1 is equal to that obtained by the electrochemical method in formamide solution.[3] The interpretation of the esr spectra is straightforward owing to the symmetry of the molecules involved; the hyperfine splittings of hydrogens and nitrogens are reported in Table I and a sample spectrum is given in Figure 1.

While there is no problem in assigning the splitting constants in the radicals I and II, the assignment of the a_H's to the two pairs of hydrogens in III is not straightforward because of the closeness of the two experimental values. On the contrary, the smaller of the two a_N splittings of III can be assigned to the nitrogens at posi-

(1) (a) Laboratorio dei Composti del Carbonio Contenenti Eteroatomi; (b) Institute of Organic and Industrial Chemistry, University of Bologna.
(2) (a) A. Carrington and J. D. Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962); (b) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).
(3) F. Gerson and W. L. F. Armarego, *Helv. Chim. Acta*, **48**, 112 (1965).
(4) J. C. M. Henning, *J. Chem. Phys.*, **44**, 2139 (1966).
(5) J. A. Pedersen and L. T. Muus, *Mol. Phys.*, **16**, 589 (1969).
(6) P. Cavalieri d'Oro, R. Danieli, G. Maccagnani, G. F. Pedulli, and P. Palmieri, *ibid.*, **20**, 365 (1971).
(7) C. L. Talcott and R. J. Myers, *ibid.*, **12**, 549 (1967).
(8) L. Lunazzi, A. Mangini, G. F. Pedulli, and F. Taddei, *J. Chem. Soc. B*, 163 (1970).
(9) B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).
(10) R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *ibid.*, **51**, 1765 (1969).