TABLE II: Total Energies (in hartrees) of the Ground State of $(CO_2)_2$ and the Ground and Excited States of $(CO_2)_2^+$, Vertical Ionization Potentials (in eV) for the States of $(CO_2)_2^+$, and Excitation Energies (in eV) for the Excited States of (CO2)2+ with Respect to the Ground X2B, State^a

	band	state	E _{CI} ^b	$I_{\mathbf{v}}[(\mathrm{CO}_2)_2]^c$	$T[(\mathrm{CO}_2)_2^+]^d$
(CO ₂),		Χ̃¹Α,	-375.0627		
$(CO_2)_2^+$	а	$ ilde{X}^2 extbf{B}^{\circ}_{u}$	-374.5643	13.562	0.0
	b	òB₀	-374.5608	13.659	0.097
	c	$\mathbf{\tilde{B}}^{2}\mathbf{A}_{u}^{\mathbf{r}}$	-374.5601	13.677	0.115
	d	ȲA	-374.5567	13.771	0.209

^a The nuclear configuration is fixed to the equilibrium geometry of the neutral dimer in Figure 5. ^b Energy determined by the MRSD-CI method. ^cVertical ionization potential calculated from the difference between the total energy of $(CO_2)_2$ and that of $(CO_2)_2^+$. ^dExcitation energy calculated from the difference between the total energy of $(CO_2)_2^+(\tilde{X}^2B_u)$ and that of the excited state of $(CO_2)_2^+$.

of $(CO_2)_2^+$ because of their instability to a spacial symmetry breaking. That is, the wave functions representing the asymmetric $(CO_2 - CO_2^+)$ electronic configurations gave lower energies than the symmetry-adapted wave functions. This finding shows that at least two electronic configurations are required to describe the electronic states of $(CO_2)_2^+$.

We therefore carried out the multireference configuration interaction (CI) calculations to obtain reliable energies of (CO₂)₂ and $(CO_2)_2^+$. We constructed the CI wave functions which involve all single and double excitations from the reference configurations for respective states (MRSD-CI method). Here, the lowest 10 orbitals were fixed to be doubly occupied. We chose the HF configuration as the reference for the neutral state. For the ionic states, two configurations were taken as discussed above. The one-particle basis functions for the CI wave functions were obtained by the 17 configuration pair type MCSCF method for the neutral state. The A_k method with the threshold value of 10 μ hartrees was applied to reduce the number of configurations in the CI wave functions and the extrapolation was performed. The

weights of reference configurations in the total wave functions were more than 88% and 85% for the neutral and ionic states, respectively. For the CI calculations, the table-MRDCI program developed by Buenker et al. was used.^{26,27}

Table II shows total electronic energies of the ground state of $(CO_2)_2$ and the ground and first three excited states of $(CO_2)_2^+$. Calculated $I_v[(CO_2)_2]$ values are given in the fifth column. Excitation energies for \tilde{A}^2B_g , \tilde{B}^2A_u , and \tilde{C}^2A_g with respect to the ground $\tilde{X}^2 B_{\mu}$ state are listed in the sixth column. The ordering of the $(CO_2)_2^+$ states is certainly in accord with that predicted from the correlation of the orbitals between $(CO_2)_2$ and two CO_2 molecules (see section B). The first and the second excited states are found to be essentially degenerated as expected from a weak interaction between the out-of-plane CO₂ $1\pi_g$ orbitals. The \tilde{X}^2B_u state lies ~0.1 eV below the \tilde{A}^2B_g state, and the \tilde{C}^2A_g state lies ~0.1 eV above the \tilde{B}^2A_u state. Ab initio calculations of $(CO_2)_2$ and $(CO_2)_2^+$ thus support our assignment in Table I made for the three peaks which appear to have ~ 0.1 eV energy spacings in the PEPICO spectrum.

It should be noted that there remains uncertainty with regard to the ionization potential for the \tilde{C}^2A_g state, since peak 3 could be the result of the dissociation of $(CO_2)_2^+$ instead of reflecting the vertical transitions to this ionic state (see section A). There is a need for further PEPICO studies under improved experimental conditions, i.e., better energy resolutions and/or greater $R_{\rm TC}/R_{\rm FC}$ ratios, in order to obtain a more reliable $I_{v}[(CO_{2})_{2}]$ value.

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Stereochemical Consequences of Halogen Atom Substitution. 1. Rotational Conformer Effects in Gaseous Diastereomeric 2,3-Dihalobutanes

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The stereochemical consequences of translationally excited 38 Cl-for-X (X = F, Cl) substitution in (2S,3R)-meso- and (2S,3S)-dl-difluorobutane, (2S,3R)-dl- and (2S,3S)-dl-chlorofluorobutane, and (2S,3R)-meso- and (2S,3S)-dl-dichlorobutane were studied in the gas phase. Although retention of configuration was determined to be the dominant substitution pathway, substantial inversion product yields were observed in all cases. A comparison of these yields revealed that the (S,R) configuration within each set always gave a smaller yield of the inverted product than the (S,S) configuration. This observation was consistent with the hypothesis that back-side substitution was a direct mechanism and that steric hindrance to such attack was subject to differences in the rotational conformer populations within each substrate configuration. In contrast, the measured yields of retention products were insensitive to substrate configuration.

Introduction

Several studies performed in the gas phase can be found in the literature dealing with the subject of the stereochemical consequences of hot $(S_{HH}2)$ homolytic bimolecular halogen-for-halogen substitutions in molecules possessing either multiple¹⁻⁷ or single⁸⁻¹² asymmetric centers. Noteworthy are the early studies of Rowland

and co-workers³⁻⁵ on halogen-for-halogen substitution in mesoand dl-1,2-dichloro-1,2-difluoroethanes and in meso- and dl-

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2,3-dichlorobutanes. Results from these studies showed that substitution occurred predominantly with retention of configuration. These authors³⁻⁵ suggested that the substitution reaction proceeded by front-side attack and that the mechanism involved direct replacement that occurred on a time scale comparable to molecular transit times for the energetic recoil atoms, in accordance with an impact model.¹³ They attributed the small amounts of radioactive inversion products that were observed predominantly to secondary radical recombination reactions induced by the high-radiation fields. However, these authors did point out that small yields of these products were always detected in amounts larger than could be accounted for simply through radiation effects and in fact that such yields could have been genuine, arising from energetic substitution with inversion.

Additional studies carried out in the gas and liquid phases by Stöcklin and co-workers⁶ on ³⁸Cl-for-Cl substitution in the diastereomeric dichlorodifluoroethanes led to a postulated two-channel mechanism for hot atom substitution: one channel involving direct replacement with retention of configuration and another channel involving formation of a highly excited complex with a lifetime sufficient to allow inversion of configuration to occur. This concept was a paradox in that while the internuclear motions within such a complex would most likely have activation barriers that could certainly be satisfied in a hot atom experiment of this nature, the lifetime of the complex in the gas phase would not be long enough to allow such motions to occur. However, this contention was in fact consistent with Stöcklin's findings, that while the yields of the retention products were subject to changes in target pressure for gas-phase experiments, the yields of inversion products were not. Of course, complex formation might be a viable pathway in liquid-phase experiments because solvent cage effects could stabilize such a complex sufficiently to allow such motions to occur. Still, the observation of inverted products in the gas phase remained an issue over the years.

Additional fuel for feeding this controversy appeared in the series of gas-phase studies by Wolf, Rack, and co-workers⁸⁻¹² on halogen-for-halogen substitution in molecules with single chiral centers. The striking feature in all of the latter studies was that not only did they observe substantial amounts of inversion products but, in many instances, the inversion product yields were actually greater than the retention products. This lead to a postulate that substitution could occur by one of two direct replacement mechanisms that would yield products with either retention or inversion of configuration, depending on whether the displacing agent attacked the front-side or back-side of the asymmetric carbon site.

An important question is whether systematic differences exist between molecules with single and multiple asymmetric carbon centers that could account for such drastic differences observed in the reaction stereochemistry. The present study was undertaken in order to obtain evidence in support of a direct inversion channel arising from back-side attack at the chiral carbon atom. Extensive gas-phase studies were carried out on ³⁸Cl-for-X (X = F, Cl) substitutions in (2S,3R)-meso- and (2S,3S)-dl-difluorobutanes (DFB's), (2S,3R)-dl- and (2S,3S)-dl-chlorofluorobutanes (CFB's), and (2S,3R)-meso- and (2S,3S)-dl-dichlorobutanes (DCB's).

Experimental Section

Materials. A diastereomeric mixture of 2,3-difluorobutane (DFB) was prepared from 2,3-butanediol by a previously reported

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method^{14,15} as described here. 2,3-Butanediol (K & K Chemical Co.) was converted to 2,3-bis(p-toluenesulfonoxy)butanes in about 75% yield by slowly adding pyridine (0.888 mol) to a mechanically stirred mixture of isomeric 2,3-butanediol (0.111 mol) and ptoluenesulfonyl chloride (0.247 mol). After several hours, the mixture was poured into 300 mL of ice water. The suspension was shaken for 5 min and, after neutralization of the residue pyridine with a dilute sulfuric acid, extracted with 100 mL of ether. The organic solution was washed with 2 N sulfuric acid, ice cold 2 N potassium hydroxide, and ice water, respectively. The ethereal solution was dried over anhydrous sodium carbonate, and the solvent was evaporated under vacuum. A white solid product was isolated as isomeric 2,3-bis(p-toluenesulfonoxy)butanes and was later identified by its NMR spectrum. Meso- and dl-2,3-DFB were prepared from the 2,3-bis(p-toluenesulfonoxy)butane (0.022 mol) mixed with anhydrous potassium fluoride (0.305 mol) and 45 mL of diethylene glycol. This step of the synthesis was carried out in a round-bottom flask equipped with a Vigreaux column. The mixture was continually stirred while the temperature was slowly raised to approximately 120 °C with the pressure being maintained at 15 Torr. Gas evolved at about 50 °C and was promptly collected in a liquid nitrogen cooled trap. Analysis of the product was carried out with a GLC having a column packed with 15% di-n-decyl phthalate (DDP) on Chromosorb P. Three peaks were identified as 2-butyne, meso-2,3-DFB, and dl-2,3-DFB. GLC assignments were initially made based on earlier work by Speranza et al.¹⁶ and were confirmed by GCMS and IR analysis.

(2S,3R)-dl-Chlorofluorobutane and (2S,3S)-dl-chlorofluorobutane (CFB) were prepared through the net addition of ClF across the double bonds of trans- and cis-2-butenes, respectively.^{17,18} The chloride ion source was N-chlorosuccinimide (0.06) mol), while the fluoride ion source was HF in pyridine (20 mL). Both reagents were purchased from Aldrich Chemical Co. The above reagents were mixed along with 30 mL of 2,3,4,5-tetrahydrothiophene 1,1-dioxide in a 300-mL stainless steel tank. The mixture was cooled to -150 °C and allowed to stand for 30 min without mixing. Either trans- or cis-2-butene was then condensed into the reaction vessel. The vessel was sealed and allowed to warm gradually (2-3 h) to ambient temperature. It was then depressurized in a controlled manner while the contents were collected in a liquid nitrogen cooled trap. Once the pressure equilibrated to atmospheric conditions, additional transfer was facilitated by vacuum transfer. After the completion of the step, the trap was allowed to stand open to the air while it warmed to ambient temperature; this dispelled any warmed unreacted butene. Approximately a 50% yield of the 2,3-CFB was obtained through this procedure. The isomers were identified by GCMS, IR, and NMR and were found to possess a 99.9% purity for the (2S,3R)-dl isomer and 98.9% purity for the (2S,3S)-dl isomer. Only traces of 2,3-dichlorobutanes and 3-chloro-2-butanol were found to be present.

meso-Dichlorobutane and dl-2,3-dichlorobutane (DCB) were obtained from an isomeric mixture that was commercially available in 90% purity (Columbia Organic Chemical Co., Inc.). The mixture was subjected to preparative GLC with use of either the column described above (DDP) or a column packed with 10% tricresyl phosphate (TCP) on Chromosorb P.

Target gases were purchased from Matheson Gas Co. They included neon (99.999% purity) and 1,3-butadiene (99% purity), both of which were used without further purification. Dichloromethane (AR Grade) was purchased from Mallinckrodt Corp. and was redistilled prior to its use.

Sample Preparation. The samples were prepared, with standard vacuum-line techniques, by introducing the desired amount of substrate into quartz ampules of 7-8-mL volumes so that a partial

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 TABLE I: Distribution of Identified ³⁸Cl-Labeled Organic Products in Gas-Phase 2,3-Dihalobutane Systems^a

labeled	absolute product yield (%) for various dihalobutane substrates			
product	DFB ^b	CFB ^b	DCB ^b	
CH ₃ Cl	2.0 ± 0.1 1 4 ± 0 3	1.9 ± 0.1	0.3 ± 0.05	
DCB	1.4 ± 0.5	0.5 ± 0.3 0.6 ± 0.2	0.9 ± 0.3	

^a Abbreviations: DFB = 2,3-difluorobutane; CFB = chlorofluorobutane; DCB = 2,3-dichlorobutane. ^b All values listed are the average for the two isomeric forms of the substrate.

pressure of 30 Torr would be exerted when the sample was heated to 65 °C during irradiation. For the 2,3-DFB systems, 100 Torr of dichloromethane was also mixed with the substrate and served as the ³⁸Cl precursor. For radiation scavenger studies, butadiene in a 2:3 ratio with respect to the substrate was employed.

Sample Irradiation. The studies were carried out using the Omaha Veterans Administration Medical Center's TRIGA reactor. The reactor was operated at a thermal neutron flux of 1.1 $\times 10^{11}$ neutrons cm⁻² s⁻¹. The irradiation dose rate, due mainly to the presence of γ radiation, was 3.0×10^{17} eV g⁻¹ m⁻¹. Sample irradiation times were varied from 5 to 60 min in order to evaluate possible radiation damage. During irradiation, samples were maintained at 65 °C, thus ensuring the substrate remained in the gas phase.

Radioassay and Absolute Yield Measurements. After irradiation, the gaseous constituents of the target were condensed with liquid nitrogen and dissolved in dichloromethane after breaking the sealed quartz vials. Aliquots of the above solution were taken with use of a liquid syringe and subjected to radiogas chromatography for separation and measurement of the labeled dihalobutane products. The dihalobutane products were identified by comparison of their elution times with those of authentic samples on three different columns: $10.4\text{-m} \times 6.4\text{-mm-o.d.}$ copper column packed with 10% tricresyl phosphate (TCP) on Chromosorb P (80–100 mesh); 9.0-m $\times 6.4\text{-mm-o.d.}$ copper column packed with 27% DC-710 with 3% stearic acid on Chromosorb P (80–100 mesh); and a 5.0-m $\times 6.4\text{-mm-o.d.}$ copper column packed with 15% di-*n*-decyl phthalate on Chromosorb P (60–80 mesh). The product analysis was carried out exclusively on the TCP column.

Labeled products eluting from the chromatography column were trapped in glass tubes packed with 40/60-mesh activated charcoal. Radioactivity for each trapped product was measured with a NaI(Tl) detector. The activity was corrected for detector efficiency, detector background, and sample fraction. The $H^{38}Cl$ yields in the irradiated samples were determined by employing a stripper similar to that described in the literature.¹⁹ At least six separate determinations were made for each experimental condition.

The total chlorine activity in the gas phase was determined for each sample by removing a known fraction of the target contents that remained dissolved in dichloromethane after the freezing step and assaying in a NaI(Tl) detector. After radioactive decay and fraction corrections were made, a measure of the total volatile activity (TVA) was obtained. The quartz ampules were also washed at least two times with NaHSO₃ solution to remove most of the nonvolatile ³⁸Cl activity from the wall of quartz ampules. Aliquots were also counted in the same fashion as described above. This measurement depicted the level of nonvolatile activity (NVA) in the target. The total ³⁸Cl activity (TA) was calculated as the sum of the TVA and NVA. The fraction of product yields was then calculated by dividing the corrected product activities by TA.

Results

The distribution of 38 Cl-labeled products in the DFB, CFB, and DCB systems are listed in Table I. The absolute yields of substitution products retaining the intact carbon skeleton ranged from 0.9% to 1.5% in all of the systems studied. The only other organic

TABLE II: Percent Retention of Configuration with 38 Cl-for-F and 38 Cl-for-Cl Substitutions at the Chiral Carbons of *meso*- and *dl*-Difluorobutanes, (2S,3R)- and (2S,3S)-*dl*-Chlorofluorobutanes, and *meso*- and *dl*-Dichlorobutanes in the Gas Phase^a

	% retention of configuration ^{b,c}		
substrate	³⁸ Cl-for-F	³⁸ Cl-for-Cl	
(2S,3R)-meso-DFB	93 ± 2		
(2S,3S)-dl-DFB	91 ± 2		
(2S,3R)-dl-CFB	85 ± 2	85 ± 2	
(2S,3S)-dl-CFB	75 ± 6	81 ± 2	
(2S,3R)-meso-DCB		89 ± 4	
		95 ^d	
(2S,3S)-dl-DCB		79 ± 6	
		0.24	

^{*a*} Abbreviations: DFB = 2,3-difluorobutane; CFB = chlorofluorobutane; DCB = 2,3-dichlorobutane. ^{*b*} Errors reported represent standard deviations of at least three independent experimental runs. ^{*c*} Percent retention values are reported from samples irradiated at a thermal neutron flux of 1.1×10^{11} neutrons cm⁻² s⁻¹ for 10 min. ^{*d*} Data from ref 4.

product identified in these systems was $CH_3^{38}Cl$. Its yield was approximately 2% in the DFB and CFB systems but significantly smaller in the DCB system. As expected from previous studies,¹⁹ the major product in all the systems was $H^{38}Cl$, which was formed by hydrogen atom abstraction. Unfortunately, we did not find the stripping column method for measuring ³⁸Cl yields reproducible. In fact, $H^{38}Cl$ yields in all systems ranged anywhere from 70% to 90% by this method.

The percent retentions of configuration for 38 Cl-for-F and 38 Cl-for-Cl substitution at the asymmetric carbon atoms in DFB, CFB, and DCB are listed in Table II. The results show clearly that halogen atom substitution proceeds predominantly with retention of configuration in all the systems. However, the results show substantial yields of inversion products in all systems, which cannot be attributed to radiation-induced processes. The presence of radiation damage and radical reactions was checked in all the systems studied by the addition of 1,3-butadiene as a radical scavenger.⁴ No statistically significant differences were noted between the scavenged and the nonscavenged systems, with the exception of the (2S,3S)-dl-dichlorobutane system, which showed slight elevation of the retention values when scavenged. In adition, the stereochemical purities of the substrates were measured after irradiation and found not to change.

Because dichloromethane was used as the ³⁸Cl precursor in the DFB system, its possible effect on the reaction stereochemistry was checked through its addition to DCB. No noticeable effect on the reaction stereochemistry could be seen.

Also listed in Table II are results found by Rowland et al.⁴ for the DCB systems. It is quite clear that the present results are similar in nature to, although different in magnitude from, these early results. That is, the (S,R) configuration within each set of substrates exhibited higher retention product yields than the corresponding (S,S) configuration. This observation was found to be statistically significant ($\geq 98\%$ confidence level) for all systems studied, with the exception of DFB. However, the same behavior was apparent even in DFB, although no reasonable statistical significance could be attached to the difference.

Absolute yields for ³⁸Cl-for-X substitutions in the 2,3-dihalobutanes are presented in Figure 1, according to the reaction type. One key observation made from this manner of presentation was that the inversion product yields exhibited no significant change between the three sets of substrates studied (i.e., DFB vs CFB vs DCB), while the (S,R) configuration within each set always yielded a lower inversion product yield than the corresponding (S,S) configuration. Of course, a comparison of absolute product yields between sets of substrates could be dangerous, particularly in the case of the DFB system since these targets possessed CH₂Cl₂ as an additional reagent. However, comparisons made of product yields arising from different configurations of the same substrate are valid. The behavior noted above was statistically significant in all cases (\geq 95% confidence level).

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(2S,3R)- meso -dichlorobutane



Figure 1. Percent absolute yields for retention (open bars) and inversion (hatched bars) products obtained from ³⁸Cl-for-X (X = F, Cl) substitution in diastereomeric dihalobutanes.

Discussion

Previous work by Wai and Rowland⁴ on ³⁸Cl-for-Cl substitution in diastereomeric DCB's showed that radiation damage could strongly influence the reaction stereochemistry in a way that could give rise to substantial yields of inversion products. It was their contention that secondary radical recombination reactions, induced by the high-radiation fields, were an important source for such products. This contention seemed reasonable at the time in view of the fact that addition of radical scavengers such as 1,3-butadiene resulted in a drastic reduction in the inversion product yields. However, these authors did point out that radiation damage probably was not the sole source for inversion products. In fact, it was suggested that energetic substitution with inversion could be a viable, although minor, pathway in the system. However, no conclusions could be drawn at that time regarding the exact nature of the inversion mechanism.

Another hypothesis to explain such observations suggested formation of a long-lived complex, where extensive motion among the substituent groups could allow for inversion of configuration in the resultant substitution product.⁴ The almost complete absence of inversion products seen in most early gas-phase work implied either that such motions were too slow to occur within the reaction time frame or else that the resultant molecules were too vibrationally excited that they rapidly decomposed. However, Machulla and Stöcklin⁶ observed no substrate pressure effects on the inversion product yields arising from both T-for-Cl and ³⁸Cl-for-Cl substitutions on the diastereomeric 1,2-dichloro-1,2difluoroethane molecules and concluded that hot complex formation, at least in the gas-phase work, was highly unlikely.

Even so, the exact nature of the mechanism for inversion product formation grew into a controversial issue particularly after work carried out by Wolf, Rack, and co-workers⁸⁻¹² on the single chiral carbon systems demonstrated that distinct channels existed for $S_{HH}2$ reactions yielding products with retention and inversion of configuration. One of the most convincing studies favoring a two-channel mechanism was the work of Firouzbakht et al.,12 which focused on the effect of kinetic energy on reaction stereochemistry arising from ¹⁸F-for-Cl substitution in 2(S)-(+)chloropropionyl chloride. In this instance, unmoderated recoil ¹⁸F atoms were observed to undergo substitution yielding predominant retention of configuration, while thermalized ¹⁸F atoms reacted to yield substitution products with nearly exclusive inversion of configuration. This perturbation to the reaction stereochemistry was considered convincing evidence in support of the two-channel argument where each channel had a different energy dependence. The question of whether the inverted product seen in this instance was the result of direct replacement involving back-side attack at the chiral carbon atom or it was the result of an alternate mechanism such as complex formation remained unanswered. The present study on the stereochemical consequences of the ³⁸Cl-for-X (X = \vec{F} , Cl) reactions in diastereometric



Figure 2. Newman projections depicting the rotational conformations of (2S,3R)-meso-dichlorobutane and (2S,3S)-dl-dichlorobutanes.

dihalobutanes was carried out in order to obtain a better understanding of this aspect of the S_{HH}^{2} reaction.

Two features of the present study allowed us to accomplish this task. On the one hand, great pains were taken to minimize radiation damage to samples during irradiation. Product peak activities were greatly enhanced because their separation by gas chromatography was initiated in less than 5 min from the end of the sample irradiation. For this reason, it was possible to generate enough chlorine-38 for quantitative measurements with a neutron flux that was 80 times lower than that used in the Wai and Rowland study on DCB.⁴ However, samples in the present study were irradiated for slightly longer times than those in the earlier report. Even so, no noticeable radiation damage was observed under the present conditions.

Perhaps the strongest feature of the present study is that it represents a culmination of work on three separate sets of substrate molecules. In all, six chemical systems were intercompared for mechanistic trends.

A comparison of the inverted product yields between sets of substrate molecules revealed that these yields did not change significantly as the nature of the displaced halogen atom changed. We pointed out earlier that such comparison could be dangerous when the DFB data is included. Even so, this behavior holds true in comparison of the CFB and DCB data. This observation supports the hypothesis that the inversion channel involves direct replacement and not an alternate mechanism such as complex formation. Complex lifetimes might be expected to be different for the different displaced halogen atoms and, therefore, might give rise to different inverted product yields.

Evidence for inversion through a direct back-side-attack mechanism was seen from the trend of fluctuation in the inverted product yields between different configurations of the same substrate. As pointed out earlier, the (S,R) configuration of each substrate consistently yielded a smaller amount of inverted product than the (S,S) configuration. This behavior could be explained on the grounds that steric hindrance to direct back-side attack would systematically vary because the conformer populations occupied by each substrate configuration would not be the same even in the gas phase.

Conformational effects in the gas phase are not uncommon. In fact, such effects have been cited as the cause for observed differences in measured ionization potentials of several dihaloalkane systems.²⁰

Recently, Borkar et al.^{21,22} reported rotational conformer populations for (2S,3R)-meso-DCB as anti (72%), gauche (14%),

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and gauche' (14%) and for (2S,3S)-dl-DCB as anti (41%), gauche (50%), and gauche' (9%), in a study using molecular mechanics calculations (MM2). Newman projections are shown in Figure 2, depicting these rotational conformers. It was clear from these projections that back-side attack from the opposite side of the halogen atom to be replaced could only be successful for the anti and gauche' forms of (2S, 3R)-meso-DCB and for the anti and gauche forms of (2S,3S)-dl-DCB because the neighboring methyl groups in the gauche and gauche' forms of the respective diastereomers would sterically hinder such attack. According to these calculations, the (S,R) configuration of DCB should offer greater steric hindrance to back-side attack because of the higher population of the gauche conformer. Similar behavior would be expected in the DFB and CFB systems as well. This expectation was in agreement with present findings that the (S,R) configuration consistently yielded lower inverted product yields.

On the other hand, direct front-side attack yielding a substitution product with retention of configuration should not be subject to steric hindrance by the butane backbone. Therefore, differences in the rotational conformer populations between different configurations of the same substrate should have little bearing on the retention product yields. This expectation was consistent with the findings in the present study.

Conclusion

This study presented additional evidence to support the hy-

pothesis that a two-channel mechanism is operative for S_{HH}^2 reactions occurring in molecules with multiple asymmetric centers. Furthermore, it demonstrated that the mechanism for back-side attack yielding inversion of configuration involved direct replacement, similar to what has been described for the direct front-side-attack mechanism yielding retention of configuration. This conclusion was revealed by the observation that the inverted product yields were uniformly affected by changes in the substrate configuration. This, in turn, had a direct bearing on the degree of steric hindrance to back-side attack because of differences in the rotational conformer populations. In contrast to this, the retention product yields did not exhibit a systematic dependence on substrate configuration as might be expected from direct replacement involving front-side attack.

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Registry No. (2S,3R)-meso-DFB, 53586-61-1; (2S,3S)-dl-DFB, 53586-62-2; (2S,3R)-dl-CFB, 20374-84-9; (2S,3S)-dl-CFB, 20374-85-0; (2S,3R)-meso-DCB, 4028-56-2; (2S,3S)-dl-DCB, 2211-67-8; 2,3-bis(ptoluenesulfonoxy)butane, 49662-27-3; 2,3-butanediol, 513-85-9; trans-2-butene, 624-64-6; cis-2-butene, 590-18-1; dichloromethane, 75-09-2.

Anomalous Energy Effects in Some Aliphatic and Alicyclic Aza Systems and Their Nitro Derivatives

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We have used an ab initio SCF molecular orbital approach in conjunction with the isodesmic reaction procedure to investigate anomalous energy effects in aliphatic and alicyclic aza systems. These molecules are found to be significantly stabilized, which we attribute to σ -conjugation of the nitrogen lone pairs; these are presumably delocalized to some extent through the σ -bond framework. The stabilization increases with the number of nitrogens in a series of similar molecules and is greater in cyclic systems, particularly when rings are fused. The magnitudes of the most negative electrostatic potentials of the aza nitrogens, which can be viewed as indicating the degrees of delocalization of the nitrogen lone pairs, decrease as the added stability increases. In these systems, the introduction of nitro groups also has an overall stabilizing effect, which may be due to further delocalization of σ -electrons, reflecting the strong electron-withdrawing power of the nitro group.

Introduction

In a recent computational study,¹ we have used the well-established isodesmic reaction procedure^{2,3} to show that the presence of the nitrogens in the diaza acyclic imidazoline (I) and piperazine (II) rings confers an added degree of stability to these molecules.



We attributed this to σ -conjugation of the nitrogen lone pairs.^{4,5}

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We now show that this is a general effect that applies to a large group of aliphatic and alicyclic aza systems and is even amplified by the presence of nitro substituents. These stabilizing tendencies are of particular interest because of the importance of many of these molecules as high-energy systems.

Methods and Procedure

The isodesmic reaction procedure^{2,3} is a means of studying anomalous energy effects in molecules. An isodesmic reaction is a hypothetical chemical process in which the number of bonds of each formal type remains the same on each side of the equation, but their mutual relationships are changed. Representative isodesmic reactions for cyclopentane (C_5H_{10}) and imidazolidine $(C_3N_2H_8)$ are given in eqs 1 and 2, respectively. The ΔE values

$$5C_2H_6 \rightarrow C_5H_{10} + 5CH_4 \tag{1}$$

$$4CH_{3}NH_{2} + C_{2}H_{6} \rightarrow C_{3}N_{2}H_{8} + 3CH_{4} + 2NH_{3}$$
 (2)

for reactions such as these reveal any deviations from bond energy additivity and are therefore interpreted as being due to special energy effects associated with the molecule being investigated,

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