reaction mechanisms are not yet very numerous. We note that the dissociation mechanism of the formaldehyde cation was also found[8b] to be controlled by conical intersections. This provides an indication that our discussion might be valid in the case of small polyatomic ions. For large polyatomic ions, electronic relaxation is probably fast, but vibrational randomization is not expected to be complete. Sufficient data are not available for electronically excited neutral molecules although substantial progress has been made in the analysis of the reaction mechanism of excited formaldehyde.[11]

(2) Is energy fully randomized? In spite of a tendency toward energy randomization, the share of energy received by each degree of freedom need not agree with statistical predictions.

(3) Assuming that a statistical treatment is reasonable, are current theories of unimolecular reactions applicable? The conditions of validity of transition-state theory have been discussed by Pechukas et al.[12] in terms of the properties of the potential-energy surfaces. They showed that a proper definition of the transition state requires careful consideration of the shape of the equipotentials. We cannot apply this criterion, since we did not calculate these contour maps in our work (only the reaction path is so far available). Moreover, the extension of this criterion to multidimensional potential-energy surfaces is not obvious. A detailed knowledge of the potential-energy surfaces is also required to carry out the normal mode analysis along the reaction path suggested by Miller et al.[13]

It seems to us, however, that the most urgent task is to incorporate nonadiabatic coupling (which provides novel and interesting features) into conventional transition-state theory. This has been done for spin–orbit interaction by Zahr et al.;[14] RRKM theory is recovered as a limit case. An extension to the case of conical intersections (point C of Figure 1) is in progress in this laboratory.

Acknowledgment. This work has been supported by the Belgian Government (Action de Recherche Concertée), the F.R.F.C. (research grant), and the F.N.R.S. (fellowship to C.S.).

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J. C. Lorquet,* C. Sannen, G. Raşeev
Département de Chimie, Université de Liège
Sart-Tilman, B-4000 Liège 1, Belgium

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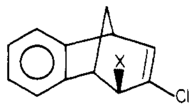
Photochemical Transformations. 29. Stereochemistry of Photorearrangements and Photosolvolyses in Some Dibenzobicyclooctadiene and Benzotricyclooctene Systems[1]

Sir:

Photosolvolyses and the photochemical Wagner–Meerwein rearrangements accompanying them upon irradiation of certain bridged ring systems containing aromatic rings and good nucleofugal groups have been of interest in this laboratory for some time.[1-4] We have recently[1,4] described our results on the homobenzyl allylic epimeric pairs **1**-Cl/**2**-Cl and **1**-OMs/**2**-OMs, which show remarkably little difference between epimers in photoreactivity or in product formation in their photorearrangements to **3** isomers or in their photosolvolyses to **1** species.



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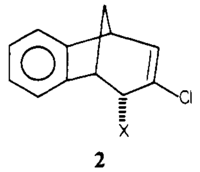

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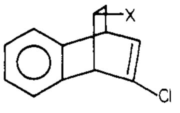

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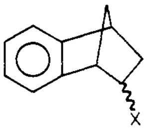

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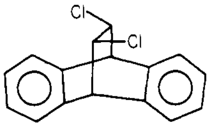
In contrast, we now report data on homobenzyl, but nonallylic systems, which do have stereochemical requirements for photoreactivity and preferences for reactions in that (a) the excited chromophore must be anti to the nucleofuge and (b) the major migrating ring is that syn to the nucleofuge. Although these results were not anticipated, a recent report[5] on the 2-benzonorbornenyl system **4** describes a similar large anti preference for photoreactivity.

Irradiation at 254 nm of the trans dichloride **5** in acetic acid gave, as major products, the rearranged dichlorides **7**-Cl and the corresponding chloroacetates **7**-OAc in about 75% yield, while compounds **8**-Cl and **8**-OAc were produced in about 25% yield. **7**-Cl and **8**-Cl photosolvolyze more slowly than they are formed. Irradiation of the cis dichloride **6** gave the same products, but in a reverse ratio. Thus the major products of photorearrangement and photosolvolysis are the result of syn migration, rather than those of the clean anti migration seen[6] in ground-state solvolyses.



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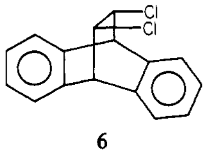

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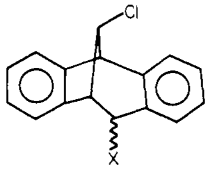

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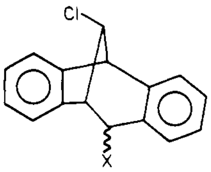

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That the photorearrangements are not radical processes may be inferred from the accompanying photosolvolyses and from experiments in which the radical chain[7] reductions of **5** and **6** with tri-*n*-butyltin hydride gave identical (approximately equal) amounts of **7**-H and **8**-H.

The stereochemical requirements of the photoreactions are revealed to a greater extent with compound **9**. Irradiation in acetic acid at 300 nm (**5** is transparent at this wavelength) led to **10** epimers as the major products. Thus the chlorine anti to the excited dimethoxybenzo chromophore leaves, while the (unsubstituted) ring syn to the nucleofuge migrates, opposite to the ground-state solvolysis which gave **11** acetates as the sole observed products.

Stereochemical requirements were also seen in the photoreactions of **12** and **13** chlorides and methanesulfonates. Irradiation of **12** at 254 nm in aqueous acetonitrile gave efficient photorearrangements to the benzylic isomers **14** and photosolvolyses to **14**-NHCOCH$_3$ and **14**-OH. Despite irradiation times 20–50 times longer, the epimeric compounds **13**-Cl and **13**-OMs were photoinert (except for the formation of small amounts of

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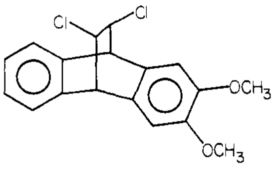
uncharacterizable materials). Thus these cyclopropylcarbinyl to homoallyl systems (which are also homobenzyl) also require an anti position relationship between chromophore and nucleofuge.



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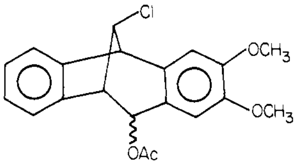

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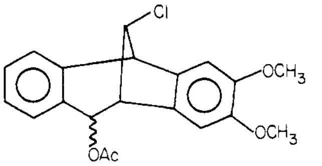

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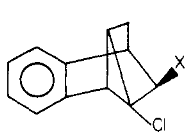

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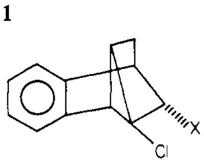

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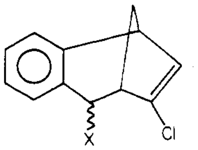
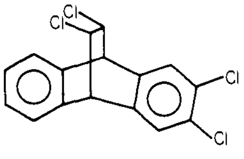


14

Similarly, irradiation of **15** in acetic acid at 285–290 nm (where **6** is transparent) gave [3.2.1] photosolvolysis and photorearrangement products **17**, while the isomeric cis dichloride **16** did not react similarly.



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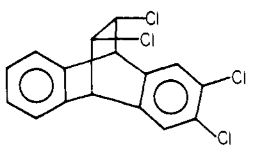

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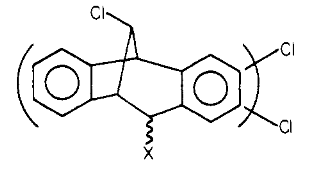

17

These photoreactions, unlike those reported earlier,[1,4] clearly require that the nucleofuge be positioned anti to the chromophoric aromatic ring. Although this is, in a sense, like the stereochemical requirements for similar ground-state reactions, [6,8] anchimeric assistance by the anti ring in the ground-state reaction is accompanied by participation of that ring in the Wagner–Meerwein rearrangement,[8] while in these photochemical reactions, we observe largely migration of the syn ring. We envisage the "anti" activation as an intramolecular electron transfer[1,4,9] which occurs from the excited (π–π^*) state of the aromatic ring to the σ^* orbital of the carbon–nucleofuge bond[10,11] to give a zwitterionic diradical. The mode by which this species decays to an ion pair with predominant syn migration of the unactivated ring or with ring opening of the cyclopropyl ring in **12** to give the observed products remains unclear.

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Stanley J. Cristol,* Robert J. Opitz
Thomas H. Bindel, Wayne A. Dickenson
Department of Chemistry
University of Colorado
Boulder, Colorado 80309

Received June 27, 1980

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[10] Examination of molecular models shows that the σ^* orbital is close to the π system of the anti aromatic ring.

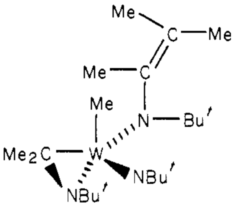
[11] Another possibility is that the activating electron occupies an orbital which combines the overlapping π^* and σ^* orbitals.

Reaction of *tert*-Butyl Isocyanide with Hexamethyltungsten. Synthesis and X-ray Crystal Structure of $\mathrm{\overline{WN(Bu^{t})CMe_{2}}(Me)(NBu^{t})\{N(BU^{t})(CMe{=}CMe_{2})\}}$

Sir:

Isocyanides are known to insert into transition-metal–alkyl bonds to give acylimidoyl, MC(R)=NR′, metal complexes;[1,2] coupling of the ligands via C–C bond formation between adjacent ligands has also been observed.[1,3] However, there are no reports of reactions in which the C–N bond of the CNR group is cleaved yielding a metal organoimido, M=NR, group[4] with concomitant C–C bond formation between carbon atoms of the CNR groups.

The interaction of hexamethyltungsten[5] in isopentane–diethyl ether at −78 °C with excess *tert*-butyl isocyanide yields yellow air-stable crystals, soluble in petroleum ether of $\mathrm{\overline{WN(Bu^{t})CMe_{2}}(Me)(NBu^{t})[N(Bu^{t})(CMe{=}CMe_{2})]}$(**1**). Analytical and spectroscopic data[6] are compatible with the structure determined[7] by X-ray diffraction (Figure 1). The unique five-coordinate tungsten(VI) complex contains CH_3, NBu^t, η^2-NBu^tCMe_2, and an unusual dialkylamido $N(Bu^t)(CMe{=}CMe_2)$ group all bound to tungsten.



1

Although the detailed mechanism of this transfer reaction, which involves transfer of five methyl groups, is not known, it seems reasonable to assume that transfer to coordinated isocyanide leads first to a $WC(Me){=}NBu^t$ group.[1,2] Migration of a second methyl group on to the carbon atom will lead to an azatungsten cyclopropane unit as found in **1** (eq 1).

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[6] Calcd: C, 48.18; H, 8.60; N, 8.03. Found: C, 48.28; H, 8.74; N, 8.04. Mp 128–129 °C; mol wt calcd 523, found 520 ± 50 (benzene); ^{1}H NMR (C_6D_6, 250 MHz) δ 1.92 (s, 3 H), 1.87 (s, 3 H), 1.73 (s, 3 H), 1.47 (s, 9 H), 1.46 (s, 9 H), 1.43 (s, 3 H), 1.28 (s, 9 H), 1.25 (s, 6 H). Apart from the *Bu*^{t} groups the other peaks in the spectrum cannot be assigned with certainty. However, the two sharp singlets at δ 1.92 and 1.87 may be due to the two nonequivalent $\overline{\mathrm{WNBu^{t}}}\mathit{CMe}_2$ methyls. (A chemical shift of δ 1.88 was assigned to Me in the $\overline{\mathrm{WNEt}}\mathrm{CH}\mathit{Me}$ group of an unisolated W^{VI} complex.[8])

[7] The structure was solved and refined by using 4069 observed [$I > 1.5\sigma(I)$] data (out of 4417 measured) recorded on a Nonius CAD4 diffractometer using Mo Kα radiation. Crystal data are a = 8.829 (2) Å, b = 10.265 (1) Å, c = 14.324 (5) Å, α = 90.87 (2)°, β = 101.47 (2)°, γ = 82.44 (2)°, space group $P\bar{1}$, Z = 2, D_c = 1.38 g cm^{-3}, and μ(Mo Kα) = 43.84 cm^{-1}. R = 0.056 with all nonhydrogen atoms anisotropic.