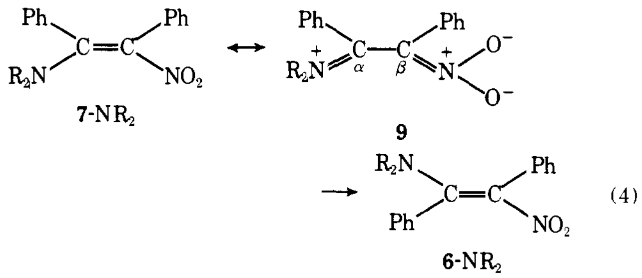
Table I. Stereochemistry of the Substitution of $PhC(I){=}C(NO_2)Ph$

substrate	nucleophile[a]	solvent	reaction conditions h/°C	% product[b]	mp of product °C
6-I	p-$MeC_6H_4S^-$	EtOH	1/25	93 **6**-SR	125–127
7-I	p-$MeC_6H_4S^-$	EtOH	1/25	91 **6**-SR	125–127
6-I	SCN^-	MeCN	96/25	89 **6**-SCN	196
7-I	SCN^-	MeCN	168/25	41 **6**-SCN	196
6-I	N_3^-	MeOH	24/0	78 **8**	118[c]
7-I	N_3^-	MeOH	24/0	75 **8**	118[c]
6-I	piperidine	MeCN	2/25	90 **6**-NR_2	172–173
7-I	piperidine	MeCN	2/25	90 **6**-NR_2	172–173
6-I	morpholine	MeCN	12/25	90 **6**-NR_2	213–214
7-I	morpholine	MeCN	12/25	90 **6**-NR_2	213–214

[a] [Nucleophile]/[substrate] = 10 except for the reactions of p-$MeC_6H_4S^-$ when the ratios were 1. [b] Yield of the isolated product. [c] Lit.[18] 117 °C.

The kinetics gave excellent first-order rate coefficients and, since **6**-I and **7**-I react with different rates,[17] a **6**-I $\rightleftharpoons$ **7**-I isomerization did not take place during the reaction. **7**-I is less stable than **6**-I as shown by the conversion of **7**-I into 100% **6**-I in the presence of one crystal of iodine in EtOH for 1 week at room temperature. When 1 equiv of **6**-I was reacted with 0.5 equiv of p-$MeC_6H_4S^-$ in ethanol, the NMR after normal workup was consistent with that of a mixture of **6**-I and **6**-SR with no evidence for **7**-I. A **6**-I $\rightleftharpoons$ **7**-I isomerization under these conditions is therefore excluded.

The stereoconvergence with morpholine and piperidine probably has no relevance to our mechanistic problem since the (Z)-nitroenamines **7**-NR_2 are expected to be configurationally unstable owing to a low rotational barrier around the C_α-C_β bond in the dipolar structure **9** (eq 4).[2,19] Stereoconvergence is generally found for this reason for substitution by amines[2,20] (except for ethylenimine).[21] The possibility that similar low rotational barriers may be responsible for the stereoconvergence for the thionucleophiles cannot be ruled out unequivocally. However, the thio substitution products of less activated electrophilic olefins are usually configurationally stable.


7-NR_2

9

6-NR_2

(4)

An initial electron transfer from the thio nucleophile, followed by combination of the formed radical anion with the thio radical to give **2**, is another possibility for our α-nitrobenzyl system.[22] Stereoconvergence is then expected at the radical-anion stage,[22b] but, since this step is assumed to be reversible and **6**-I $\rightleftharpoons$ **7**-I isomerization during the reaction was not observed, this route is unlikely. The use of less ambiguous, but slower nucleophiles, such as CF_3COO^- is currently under study.

In conclusion, the present first example of stereoconvergence under kinetic control[23] in substitution of an activated halo olefin (X ≠ F) by nonamine nucleophiles strongly supports other evidence for the multistep substitution route, at least for highly activated systems.

Acknowledgment. We are indebted to Professor V. D. Parker for helpful discussions.

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An Experimental Study of Nucleophilic Addition to Formaldehyde in the Gas Phase

Sir:

The addition of nucleophiles to carbonyl compounds has long played a vital role in organic chemistry.[1] The adducts themselves have rarely been sufficiently stable to be observed or isolated but are commonly invoked as "tetrahedral intermediates" in the mechanisms of important transformations in solution.[2,3] More recently several attempts have been reported to identify and assess the role of such intermediates in analogous gas-phase anion-molecule reactions. These attempts were carried out at low pressures ($<10^{-4}$ Torr) and for adducts which again almost invariably acted as transient species.[4] Here we report results of gas-phase measurements of reactions of several simple nucleophiles with the simplest carbonyl system, formaldehyde, at higher pressures (~0.5 Torr).[5] They provide the first direct observation of stabilized nucleophile-formaldehyde adducts including the simplest adduct with H^- whose formation has recently been supported theoretically.[6] Furthermore, they provide examples of carbonyl additions which yield intermediates that undergo further transformation. The intrinsic behavior of these addition reactions, which are so fundamental to solution chemistry, has been fully characterized through the identification of products and the measurement of reaction kinetics.

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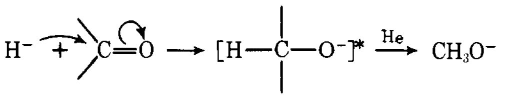
Table I. Summary of Rate Measurements for Reactions of Nucleophiles with Formaldehyde in the Gas Phase at 297 ± 2 K

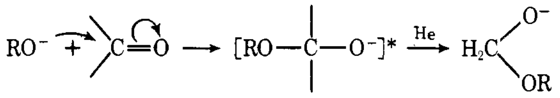
reaction	k^a
$H^- + CH_2O + He \rightarrow CH_3O^- + He$	$(2 \pm 1) \times 10^{-26}$ [b] $[7.5 \times 10^{-25}]$
$OH^- + CH_2O + He \rightarrow HOCH_2O^- + He$	$(2 \pm 1) \times 10^{-26}$ [c] $[5 \times 10^{-25}]$
$CH_3O^- + CH_2O + H_2 \rightarrow CH_3OCH_2O^- + H_2$	$(9.0 \pm 0.4) \times 10^{-28}$ [c] $[4 \times 10^{-25}]$
$NH_2^- + CH_2O \rightarrow H^- + (NH_2CHO)$	$(1.9 \pm 0.5) \times 10^{-9}$ $[4.1 \times 10^{-9}]$
$CH_3NH^- + CH_2O \rightarrow H^- + (CH_3NHCHO)$	$(1.9 \pm 0.5) \times 10^{-9}$ $[3.4 \times 10^{-9}]$
$O^- + CH_2O \rightarrow HCO_2^- + H \rightarrow OH^- + HCO$	$(3.1 \pm 0.8) \times 10^{-9}$ $[4.1 \times 10^{-9}]$

[a] Three-body rate constants in units of cm^6 $molecule^{-2}$ s^{-1} and two-body rate constants in units of cm^3 $molecule^{-1}$ s^{-1}. The values given in brackets represent collision rate constants calculated using the AADO theory: T. Su, E. C. F. Su, and M. T. Bowers, *J. Chem. Phys.*, **69**, 2243 (1978); S. D. Tanner, G. I. Mackay, and D. K. Bohme, *Can. J. Chem.*, **57**, 2350 (1979). The three-body "collision" rate constants were taken to be equal to $k_c/[He$ or $H_2]$ where k_c is the collision rate constant for the first step in the two-step mechanism. [b] P = 0.534–0.594 Torr. [c] P = 0.26 Torr.

Hydride ion was observed to react in an inert helium bath at ~0.5 Torr to produce the methoxy ion. Recent SCF-LCGO-MO calculations of this reaction path have shown that, as H^- approaches carbon to within bonding distance, the potential energy of the system drops rapidly and C becomes tetrahedrally coordinated.[6] Energy appearing as internal vibrations of CH_3O^- is removed under our experimental operating conditions by collision with He atoms[7] so that eq 1 obtains; also


(1)

OH^- and CH_3O^- were observed to form adducts in what is likely to be an analogous fashion (R = H, CH_3) (eq 2). The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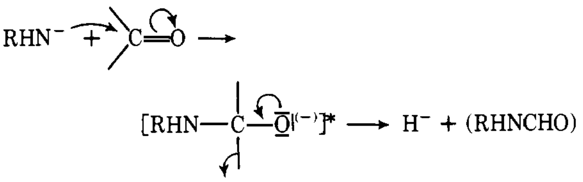
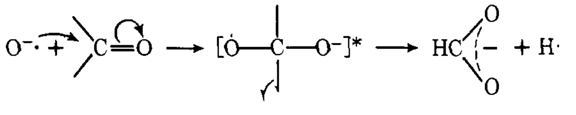
unusually large values of the rate constants for these association reactions (see Table I) are consistent with the formation of a "tight" adduct formed through chemical bonding rather than a "loose" adduct formed through proton bonding, $X^- \cdots H^+ \cdots {}^-CHO$, or simple electrostatic interaction, $X^- \cdot CH_2O$.[8]

The hydride ion was formed through the addition of amide ion to formaldehyde which is followed by elimination prior to stabilization by collision (R = H)[9] (eq 3). An analogous re-


(3)

action was observed with the methyl amide ion (R = CH_3). Both of these reactions proceed rapidly in the gas phase (see Table I) and restore the original carbonyl carbon to a doubly bonded state.[10]

Elimination was also observed to be a major reaction channel in the addition of oxide *radical* anion to formaldehyde[11] (eq 4). However, in this instance, the elimination appeared to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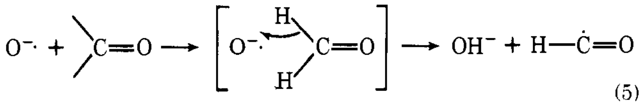
compete with H-atom abstraction which presumably proceeds prior to the formation of a truly bound tetrahedral intermediate[12] (eq 5).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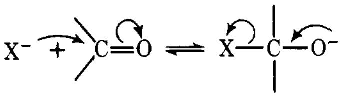
Studies are currently in progress involving reactions with other nucleophiles. Preliminary indications are that the very stable nucleophiles F^-, Cl^-, CN^-, and NO_2^- fail to produce adducts, $k \lesssim 10^{-28}$ cm^6 $molecule^{-2}$ s^{-1} at ~0.5 Torr. The heats of formation of the corresponding hypothetical tetrahedral intermediates are not known but it may be inferred from the high electron affinities ($\gtrsim$2.5 eV)[13] of these nucleophiles that the reverse reaction is likely to be preferred in these cases (X = F, Cl, CN, NO_2) (eq 6); i.e., the formation of these adducts is actually endoergic at room temperature.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In a general sense the results reported here have established a considerable diversity in the intrinsic modes of transformation of tetrahedral intermediates in nucleophilic additions of anions to formaldehyde. There is now an obvious need for further theoretical investigations and for an extension of experimental investigations to other carbonyl systems, particularly at high pressures.[14]

Acknowledgments. We thank Dr. R. van Doorn for stimulating discussions and the Natural Sciences and Engineering Council of Canada for financial support.

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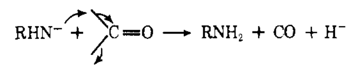
(9) We could not rule out the production of HCO$^-$ by proton abstraction under our experimental operating conditions. An ion with *m/e* 29 was observed to be produced in small quantities and shown in separate experiments to react with NH_3.

(10) As noted by one of the referees, another exothermic pathway is available for the production of H$^-$:



$$\mathrm{RHN^-} + \mathrm{{>}C{=}O} \longrightarrow \mathrm{RNH_2} + \mathrm{CO} + \mathrm{H^-}$$

(11) The formation of H$^-$ could not be precluded under our experimental operating conditions because of its known associative detachment reaction with O_2 which was present in the reaction region; see D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **53**, 987 (1970).

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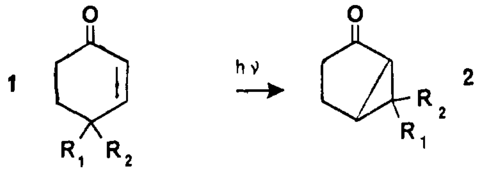
Photochemistry of Ketones in Solution. 57.[1] Synthesis and Photochemistry of a Constrained 2-Cyclohexenone[2]

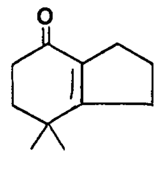
Sir:

The excited-state properties of 2-cyclohexenones continue to interest organic, physical, and theoretical chemists.[3] We have previously argued that the very low quantum efficiency ($\phi \leq 0.01$) of the so-called "lumiketone rearrangement" of 4,4-dialkyl enones, **1** → **2**,[4] cannot be adequately explained on the basis of a mechanism involving C—C bond scission to form diradical or zwitterionic intermediates which revert to starting material in competition with progress to product.[5]



We have suggested[3c,5] that the planar enone triplet, formed in unit efficiency from the excited singlet state(s), relaxes rapidly by twisting around the C=C bond to give a twisted species which serves as an ideal "funnel" for crossing to the ground state (S_0) potential surface from T_1, since the difference in energy of S_0 and T_1 is minimized at this geometry.[5,6] A partitioning on the S_0 surface between return to starting material and conversion into rearrangement products is postulated, the latter being the minor decay pathway.

One corollary of this description is that enones which are constrained from twisting around the C=C bond should be unable to undergo the lumiketone rearrangement and might display photochemical and photophysical properties atypical of "normal" unconstrained enones. This has now been confirmed in the case of bicyclic enone **3**, a structural analogue of an enone (**4**) which displays prototypic enone photoreactivity [i.e., inefficient rearrangement to lumiketone and cyclopentenone isomers via short-lived triplet states in *tert*-butyl alcohol (*t*-BuOH) and photoreduction in hydrogen-donor media such as 2-propanol (*i*-PrOH)].[3,7,8]



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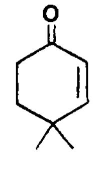

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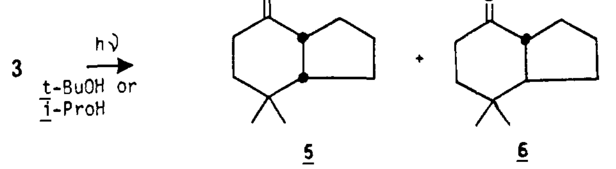
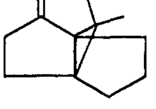
The synthesis of **3** is modeled in its initial stages on work of Raphael et al.[9] The structure of **3** is evident from spectral data, most notably λ_{max}^{EtOH} 249 nm (log ϵ 4.07); *m/e* 164 (M), 149 (M$^+$ − CH_3), 136 (M$^+$ − CO$^+$), 122 (base, M$^+$ − C_3H_6); IR (CCl_4) 1665, 1625, 1385, 1365 cm^{-1}; NMR δ 1.15 (sharp s, 6 H), 1.5–2.7 (m, 10 H), absence of vinyl H.

Irradiation of **3** in degassed *t*-BuOH through Pyrex at 300 nm led in low quantum efficiency to the formation of two major products, which were isolated chromatographically and identified as the *cis*- and *trans*-dihydro ketones **5** and **6** on the basis of spectral characteristics and independent synthesis from **3** using various hydrogenation methods.[10] The trans ketone **6** could be epimerized to the cis ketone **5** by treatment with $NaNH_2$-pyridine-Me_2SO-d_6.[11] A gas chromatography/mass spectroscopic analysis of the complete photolysate in this and all other solvents studied indicated the absence of any product isomeric with the starting enone but the presence of a minor product corresponding to an adduct of **3** and *t*-BuOH, probably **8**.[12-15] Enol **9**, synthesized independently from **3** by reduction with Dibal in toluene,[18] was not detected among the photolysis products of **3** in any solvent studied.



Φ = 0.00016 in t-BuOH
Φ = 0.041 in i-PrOH



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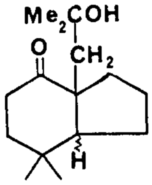

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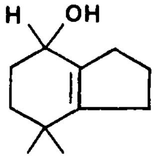

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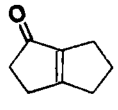

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Irradiation of **3** in 2-PrOH under similar conditions again gave **5** and **6** in greater quantum efficiency and no photoisomers. The reaction was readily quenched in the presence of 1,3-cyclohexadiene (E_T = 53 kcal/mol)[19] with $k_q\tau_T$ = 63 M^{-1}, corresponding to a lifetime of the reactive triplet excited state of ~20 ns, assuming that triplet quenching is approximately diffusion controlled at 3×10^9 M^{-1} s^{-1} in *i*-PrOH.[19] Photoreduction is also observed in acetone, leading to **5**, **6**, and 2,5-hexanedione.

The photochemical behavior of **3** is qualitatively in accord with our expectation that typical enone molecular rearrangements should be inhibited in this case because of structural rigidity. However, the triplet lifetime of **3** is not particularly enhanced relative to that of cyclohexenone[6b] and simple substituted cyclohexenone[3,4,7] triplets which are not constrained from twisting around C=C.[20] Indeed, there is now strong

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