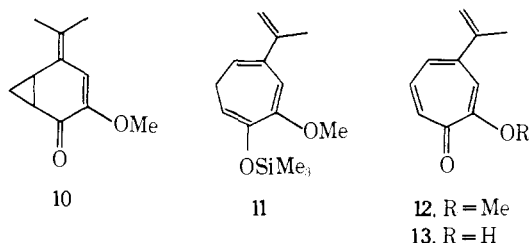


also noteworthy that spirans **8** and **9** interconvert upon being treated independently with trifluoroacetic acid. Furthermore, the observation that spiran **8** rearranges to **6** more rapidly than does spiran **9** suggests that the conversion of **5** to **6** proceeds entirely through spiran **8**. This notion is supported by the discovery that, while spiran **8** is converted to **6** (40%) upon treatment with boron trifluoride etherate in nitromethane, spiran **9** is recovered unchanged (1.0 equiv, 25 °C, 60 min). Although it is not readily apparent from an inspection of molecular models, these results indicate that only spiran **8** is able to adopt the stereoelectronic arrangement required for facile aryl migration. It is apparent that the foregoing synthetic sequence to **2** embodies sufficient flexibility to incorporate the C-7 acetamido group or its equivalent at an early stage of the synthesis.

The general utility of cyclopropyl ketone **4** as a precursor to monocyclic tropolones has been demonstrated within the context of a synthesis of β -dolabrin (**13**).¹³ Treatment of **4** with isopropylmagnesium bromide and subsequent dehydration-deketalization with acid (BF₃·Et₂O, CH₃NO₂) afforded dienone **10** (50%). Ring expansion of **10** to **11** was effected with base (KH, THF) followed by Me₃SiCl (90%). This transfor-



mation is viewed as proceeding via the electrocyclic ring opening of the enolate derived from **10**.¹⁴ Oxidation of **11** with chloranil to **12** (60–70%) and subsequent demethylation (BBr₃) afforded β -dolabrin (**13**), mp 56.5–57 °C.

Acknowledgment. Support from the National Institutes of Health is gratefully acknowledged.

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- (9) Spectral data of all new compounds reported herein are in accord with the assigned structures. All new solids gave satisfactory combustion analyses.
- (10) We wish to thank Professor S. Tobinaga for supplying us with authentic samples of (\pm)-**2** and (\pm)-**8**. Samples of **2** and **8** prepared as described herein were identical (melting point, NMR, IR, TLC) with the samples provided by Professor Tobinaga. Hydrolysis of **2** afforded desacetamidocolchicine whose spectral and physical characteristics were in accord with those reported elsewhere.^{2a}

- (11) The stereoisomeric dienones and spirans were separated by liquid chromatographic techniques.
- (12) We reason that in the cyclization reaction the aryl group will predominantly attack the convex face of the bicyclo[4.1.0] system thus affording **9** as the major product. A careful analysis of the Tobinaga synthesis,²⁹ which gives only one of the diastereomeric spirans, predicts that **8** should be produced. Also in accord with the stereochemical assignment, the cyclopropyl methylene resonates at 14.5 and 12.4 ppm relative to Me₄Si in the ¹³C spectra of **8** and **9**, respectively. A downfield shift is expected in **8** because of deshielding by the aryl group.
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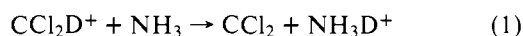
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Proton Affinity of Dichlorocarbene

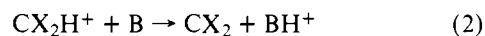
Sir:

In a recent study of Levi et al.¹ employing the bracketing proton-transfer technique, the proton affinity of CCl₂ was estimated to be ~7 kcal/mol above that of NH₃. This is in contradiction to an earlier study of the proton affinity of CCl₂ from this laboratory,² in which the proton-transfer reaction



was reported to occur with a relatively high efficiency ($k = 4.4 \times 10^{-10} \text{ cm}^3/(\text{molecule s})$). The occurrence of reaction 1 would suggest that the proton affinity of CCl₂D⁺ is lower than that of NH₃. It is possible that the cause for this discrepancy could be that, instead of the sought-after proton-transfer reactions, there occur other, energetically more favorable, competing reactions between CCl₂H⁺ and the bases (*i*-Pr₂O, *i*-Pr₂S, aniline) examined by Levi et al.,¹ even though all these compounds have proton affinities above that of NH₃.

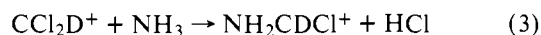
It has been shown in previous studies^{2,3} that halomethyl ions undergo a multitude of reactions with organic molecules. It is clear that the task of pinpointing the bases (B) for which the proton-transfer reaction



(where CX₂ = CF₂, CCl₂, CFCl, etc.) turns from endothermic to exothermic can only be expected to be entirely successful if energetically and sterically more favorable reaction channels are not available to the reaction pair. It will be shown here that slightly exothermic proton transfer reactions do not always occur when a favorable competing channel is available.

We wish to report new ICR data on CCl₃D–B (20:1) mixtures carried out at 325 K, a total pressure of 3–5 × 10⁻⁶, and an electron energy of 13 eV. We concentrated on the reactions with ethers, sulfides, and NH₃. The results are summarized in Table I.

The occurrence of reaction 1 was confirmed. The determination of the actual efficiency of this reaction was, as before, complicated by the occurrence of a competing reaction sequence⁸ resulting ultimately in the formation of the same product ion:



However, the occurrence of reaction 1 was verified in an experiment in which the precursors of NH₃D⁺ were individually removed from the system (CCl₃D–NH₃ = 50:1) through double resonance ion ejection.

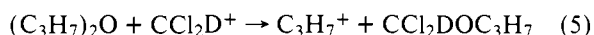
Table I. Observed Reactions and Rate Coefficients for the Reactions $\text{CCl}_2\text{D}^+ + \text{M} \rightarrow \text{Products}$

	Rel PA	Observed reactions	$k_{\text{total}} \times 10^{10a}$
$(\text{CH}_3)_2\text{O}$	-11.4 ^b	$\text{CCl}_2\text{D}^+ + (\text{CH}_3)_2\text{O} \rightarrow \text{CH}_3\text{OCH}_2^+ + \text{CCl}_2\text{DH}$	4.0 ± 1.0
$(\text{CH}_3)_2\text{S}$	-4.9 ^b	$\text{CCl}_2\text{D}^+ + (\text{CH}_3)_2\text{S} \rightarrow \text{CH}_3\text{SCH}_2^+ + \text{CCl}_2\text{DH}$	14.9 ± 2.0
$(\text{C}_2\text{H}_5)_2\text{O}$	-4.8 ^c	$\text{CCl}_2\text{D}^+ + (\text{C}_2\text{H}_5)_2\text{O} \rightarrow (\text{C}_2\text{H}_5)_2\text{OD}^+ + \text{CCl}_2$ (22%) $\rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_4^+ + \text{CCl}_2\text{DH}$ (78%)	12.5 ± 3.5
$(n\text{-C}_3\text{H}_7)_2\text{O}$	-3.2 ^c	$\text{CCl}_2\text{D}^+ + (n\text{-C}_3\text{H}_7)_2\text{O} \rightarrow \text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_7\text{OC}_2\text{H}_5$ (100%)	12.8 ± 2.5
$\text{C}_2\text{H}_5\text{SCH}_3$	-1.8 ^c	$\text{CCl}_2\text{D}^+ + \text{C}_2\text{H}_5\text{SCH}_3 \rightarrow \text{CH}_3\text{SC}_2\text{H}_4^+ + \text{CCl}_2\text{DH}$ (~100%)	
NH_3	0.0 ^d	$\text{CCl}_2\text{D}^+ + \text{NH}_3 \rightarrow \text{NH}_3\text{D}^+ + \text{CCl}_2$ (~57%) $\rightarrow \text{NH}_2\text{CDCl}^+ (\text{NH}_2\text{CHCl}^+) + \text{HCl} (\text{DCl})$ (~43%)	7.8 ± 1.5
$(i\text{-C}_3\text{H}_7)_2\text{O}$	+0.5 ^c	$\text{CCl}_2\text{D}^+ + (i\text{-C}_3\text{H}_7)_2\text{O} \rightarrow \text{C}_3\text{H}_7^+ + i\text{-C}_3\text{H}_7\text{OC}_2\text{H}_5$	13.0 ± 3.0
$\text{C}_6\text{H}_5\text{NH}_2$	+6.2 ^c	$\text{CCl}_2\text{D}^+ + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2\text{D}^+ + \text{CCl}_2$ (1%) $\rightarrow \text{C}_6\text{H}_5\text{NH}_2^+ + \text{CCl}_2\text{D}$ (99%)	10 ± 5

^a In units of $\text{cm}^3/(\text{molecule s})$. ^b Relative proton affinity derived from scales of ΔG° for various proton transfer reactions ($\text{AH}^+ + \text{B} \rightleftharpoons \text{BH}^+ + \text{A}$) at 300 K⁴ and 600 K;⁵ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta H^\circ = \text{PA}(\text{A}) - \text{PA}(\text{B})$. ^c Relative proton affinity derived from values of ΔG° reported in ref 4 and entropy changes estimated from considerations of symmetry and intramolecular interactions.⁶ ^d $\text{PA}(\text{NH}_3)$ cited in ref 5 is 202.3 ± 2 kcal/mol (taking $\Delta H_f(\text{H}^+) = 367.2$ kcal/mol). Corrections to this value necessitated by revisions of the heats of formation of standard bases and measurements of entropy changes for proton-transfer reactions⁷ and the use of a value of 365.2 kcal/mol for $\Delta H_f(\text{H}^+)$ ⁹ lead to $\text{PA}(\text{NH}_3) = 207.3 \pm 2$ kcal/mol.

As noted before, CCl_2D^+ reacts with CH_3OCH_3 exclusively via a hydride-transfer reaction. Hydride transfer also occurs in the reaction with $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. However, deuteron transfer from CCl_2D^+ is also observed as a minor channel; the occurrence of this reaction was not discerned in our earlier experiments because deuteration was not used, and the product from the relatively minor reaction with CCl_2H^+ was obscured by the presence of a large abundance of $(\text{C}_2\text{H}_5)_2\text{OH}^+$ from other reactions. The observation of this deuteron-transfer reaction means that the proton affinity of CCl_2 is actually lower than our previous estimate by at least 4.8 kcal/mol.

In contrast, in the case of $(n\text{-Pr})_2\text{O}$ and $(i\text{-Pr})_2\text{O}$, no deuteron transfer from CCl_2D^+ was observed, even though the proton affinities of these molecules lie, respectively, 1.6 and 5.3 kcal/mol above that of diethyl ether. Instead, a fast displacement reaction was observed in both cases:



In the case of the $\text{CCl}_2\text{D}^+ - (\text{CH}_3)_2\text{S}$ reaction, we confirmed our earlier observation that proton transfer does not occur, even though $\text{PA}(\text{CH}_3\text{SCH}_3) \approx \text{PA}(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)$. In this case, the competing hydride-transfer reaction is seen to be favorable. For methyl ethyl sulfide, hydride transfer is also the exclusive reaction channel.

The predominant reaction of CCl_2D^+ with aniline is charge transfer, although a small amount (~1%) of deuteron transfer was observed. The charge-transfer reaction is 17 kcal/mol exothermic,⁹ in our previous investigation of this subject,² as well as other work from this laboratory,¹⁰ it has been noted that exothermic charge-transfer reactions generally predominate over competing reaction channels even if the alternate channels are more exothermic. In this case, the proton-transfer channel is less exothermic ($\Delta H_{\text{PT}} \approx -14$ kcal/mol) than the charge transfer and would not be expected to compete.

There are several factors contributing to uncertainty in the derivation of a value of $\Delta H_f(\text{CCl}_2)$ from these results. These include (1) the near impossibility of pinpointing from such experiments (in which other fast reactions compete with proton transfer) the energy at which proton (deuteron) transfer from CCl_2H^+ (CCl_2D^+) is thermoneutral; (2) the difficulties associated with the assignment of absolute values to the proton affinity scale, and (3) the uncertainties in the heat of formation of CCl_2H^+ (CCl_2D^+). However, the results given in Table I indicate that $\text{PA}(\text{CCl}_2) < \text{PA}(\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)$. Accepting a value of 207.3 ± 2 kcal/mol for $\text{PA}(\text{NH}_3)$ (Table I, footnote d), this leads to an estimate of $\text{PA}(\text{CCl}_2) \leq 202.5 \pm 2$ kcal/

mol. Taking a value of 211 kcal/mol for $\Delta H_f(\text{CCl}_2\text{H}^+)$,¹¹ and 365.2 kcal/mol for $\Delta H_f(\text{H}^+)$,⁹ one obtains $\Delta H_f(\text{CCl}_2) \leq 47.8 \pm 2$ kcal/mol. Values in the literature for $\Delta H_f(\text{CCl}_2)$ range from 57¹² to 40 kcal/mol.^{13,14}

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Homogeneous Catalysis of the Water Gas Shift Reaction by Mixed-Metal (Iron/Ruthenium) Catalysts

Sir:

The water gas shift reaction (eq 1) is an important pathway for the formation of dihydrogen from water using the reducing equivalents of carbon monoxide. Production of H_2 via the shift reaction is a process certain to have increasing significance given the need to derive a larger fraction of energy require-