of ethane,[9] we find that Mo(0)/DA such as $Mo(CO)_6$/DA,He,500°;H_2,650° exhibits remarkable activity for the hydrogenolysis of alkanes. At 200–300 °C in runs at low conversion with a flow reactor, total flow rates of 30–400 $cm^3\ min^{-1}$, pressures of H_2 and propane of 0.96 and 0.04 atm, and usually about 4 μmol of Mo on 0.05 g of DA, reactions 1 and 2 were observed. At

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \tag{1}$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4 \tag{2}$$

250 °C on He,500°,1;H_2,650°,1, N_t was 0.070 s^{-1} initially, 0.067 s^{-1} after 1 h, and 0.064 s^{-1} after runs for 1 h each at 200 and 300 °C. Initially, $N_t(1)$ (for reaction 1) was 0.053 and $N_t(2)$ was 0.017 s^{-1}; $E_a(1)$ was 105 kJ mol^{-1} and $E_a(2)$ was 142 kJ mol^{-1}. N_t's were almost the same when 2 μmol of Mo on 0.2 g of DA was used and also with $Mo(CO)_6$/DA,He,500°,1;H_2,650°,0.5;H_2,950°,0.25. For $Mo(CO)_6$/DA which had been first treated with He,300°,1, detectable activity was exhibited after H_2,300° and activity rose steadily up to H_2, 650 °C.

The catalysts were very sensitive to contamination. In a pulse reactor at 300 °C, $Mo(CO)_6$/DA,He,500°;H_2,950° gave a conversion of 12.9% per pulse. A pulse of O_2 (O_2/Mo = 2.4) completely poisoned the catalyst for the hydrogenolysis of propane. Subsequent treatment by H_2,450° led to 0.03% conversion, H_2,650° to 3.05%, H_2,800° to 7.6%, and H_2,950° to 12.6%. A pulse of carbon monoxide (CO/Mo = 9.6) at 300 °C reduced the activity to zero and a pulse of H_2O (H_2O(adsorbed)/Mo = 1.05) led to 41% of the initial activity.[10] Even nitrogen poisoned the hydrogenolysis. A pulse with N_2/Mo = 1.3 on a catalyst containing 31 μmol of Mo reduced the hydrogenolysis from 99 to 79% and 3 more pulses reduced it to 40%. After H_2,950°, the conversion had become 100%.

As measured in the pulse reactor, the rate of hydrogenolysis of ethane was about 0.13 that of propane at 250 °C and 0.5 at 300 °C. Relative to propane, the rates for butane, pentane, and neopentane at 250 °C were 1.2, 1.7, and 0.3, respectively.

The experiments so far described started with DA. One might suspect that similar material would result from heating $Mo(CO)_6$/PDA in hydrogen to temperatures which would lead to the formation of dehydroxylated alumina. $Mo(CO)_6$/PDA,He,300°,1;H_2,650°,1;He,650°,0.25 was titrated with oxygen at 500 °C by a pulse method. The average ON calculated from the oxygen consumption assuming Mo^{6+} resulted was near +2. After exposure to H_2, 800 °C, 0.25 h, ON was zero to within an uncertainty of ±0.2. Materials so prepared were investigated for the hydrogenolysis of propane at 300 °C. After H_2,500°, N_t was about 0.001; after H_2,650°,0.011; after H_2,800°,0.34; and after H_2,950°,0.24 s^{-1}. In these experiments, one sample of catalyst was activated to successively higher temperatures. In another run, $Mo(CO)_6$/PDA,H_2,800°,0.5 gave N_t at 250 °C = 0.079 s^{-1}. Similar results were obtained in the pulse reactor.

A $MoO_3/\gamma\text{-}Al_2O_3$ containing 4 μmol of Mo per 0.05 g of alumina was prepared in the conventional fashion by impregnating alumina with ammonium molybdate followed by calcination at 500 °C. It was activated in H_2,800°,0.5. In the flow reactor this material gave N_t = 0.058 s^{-1} at 250 °C. Relative yields in reactions 1 and 2 and E_a's were close to those of activated $Mo(CO)_6$/DA as were those of $Mo(CO)_6$/PDA activated in hydrogen at 800 and 950 °C.

A few experiments have been run with $W(CO)_6$/DA. $W(CO)_6$/DA,He,300°,1;H_2,760°,1 was an active catalyst for the hydrogenolysis of propane in both reaction 1 and reaction 2 with an activity in the vicinity of that of $Mo(CO)_6$/DA with the same pretreatment.

It has not yet been possible to characterize well these Mo(0)/DA catalysts, but they might consist of molybdenum metal particles with nearly 30% exposed, supported on DA.[5] It is also probable that the Mo^{2+} present after He,300–500° is reduced to Mo(0) by exposure to hydrogen at high temperatures. We have no secure information as to the degree of interaction, if any, between Mo(0) and the support.

Sinfelt[9] reported that the highest activity for the hydrogenolysis of ethane of metals which had been studied was exhibited by ruthenium and osmium. He also reported that metallic molybdenum made by reduction of MoO_2 had only a very slight activity. From his data, N_t per Ru_s would be 0.035 s^{-1} at 250 °C under our conditions. In our work, per total Mo, N_t was 0.007 for the hydrogenolysis of ethane at 250 °C, or, if the percentage exposed of Mo is 30, N_t per Mo_s would be 0.02 s^{-1}. The origin of the apparent discrepancy between Sinfelt's work and ours is unclear. Perhaps, in the experiments of Sinfelt, MoO_2 was reduced at too low a temperature to remove surface contamination. Alternatively, the activity of our catalysts may be higher than that of bulk metallic Mo either because a much larger activity characterizes small particles of Mo or because of some kind of interaction between Mo(0) and the support.

Burch and Mitchell[11] have reported that a mixture of Mo and MoO_2 made by the partial reduction of MoO_2 is a very active catalyst for the skeletal isomerization of alkanes but a poor one for hydrogenolysis. Our catalysts exhibit a remarkably high activity for hydrogenolysis, but, even at 300 °C, activity for isomerization of butane, pentane, and hexane was negligible. In the work of Burch and Mitchell, the surfaces of particles of Mo(0) were unlikely to have been clean.

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[9] Sinfelt, J. H. *Adv. Catal.* **1973**, *23*, 91–119. See also: Boudart, M.; Oyama, S. T.; Leclerq, L. *Proc. Int. Congr. Catal. 7th* **1980**, in press. A catalyst, $Mo(CO)_6$/DA,He,500°,1;H_2,950°,0.25 gave for the hydrogenolysis of propane at 250 °C, N_t = 0.054 s^{-1}. After exposure to the stream of C_3H_8 + H_2 at 580 °C for 0.5 h and then to H_2,580°,0.08 (a treatment which might be expected to give carbiding), N_t was 0.042 s^{-1}. After H_2,950°,0.5, N_t was 0.050 s^{-1}.

[10] After CO poisoning, the catalyst still led to hydrogenation of 99% of a pulse of propylene at 25 °C. However, Mo/Al_2O_3 catalysts other than clean Mo(0)/DA are effective catalysts for several reactions. Clearly, the methanation of CO at 300 °C on $Mo(CO)_6$/DA,He,300–500° in which both CO and H_2O are present does not proceed on clean Mo(0). The rate of hydrogenolysis of cyclopropane at 60 °C on $Mo(CO)_6$/DA,He,300° is little affected by the additional pretreatment of the catalyst with H_2 at 300–950 °C, and Mo^{2+}/PDA also exhibits high activity for this reaction. However, the ratio, single/double hydrogenolysis, decreases substantially as the ON of Mo increases.

[11] Burch, R.; Mitchell, P. C. H. *J. Less-Common Met.* **1977**, *54*, 363–372.

Gas-Phase Nucleophilic Addition Reactions of Phenylnitrene Anion Radical with Certain Carbonyl-Containing Molecules[1]

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Gas-phase studies of nucleophilic addition reactions to carbonyl groups with closed-shell, singlet anions are difficult unless an anionic leaving group is present in the carbonyl compound, e.g., with acid halides,[2] esters,[3] etc. We recently reported the use of phenylnitrene anion radical ($PhN^{-}\cdot$) to observe competitive 1,2- and 1,4-addition processes with certain α,β-unsaturated molecules.[1] We now wish to report preliminary results of ion-molecule reactions of $PhN^{-}\cdot$, an open-shell, doublet reagent, with several simple carbonyl-containing compounds which establish the nucleophilic addition mechanism for adduct formation.[4]

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[1] (a) Paper 9 in the series "Hypovalent Radicals"; for paper 8, see: McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.*, **1980**, *102*, 6146. (b) Presented in part at the Fifth IUPAC Conference on Physical Organic Chemistry, University of California, Santa Cruz, CA, Aug 17–22, 1980.

[2] (a) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Asubiojo, O. I.; Blair, L. K.; Brauman, J. I. *Ibid* **1975**, *97*, 6685.

[3] (a) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049. (b) Fukuda, E. K.; McIver, R. T. *Ibid.* **1979**, *101*, 2498.

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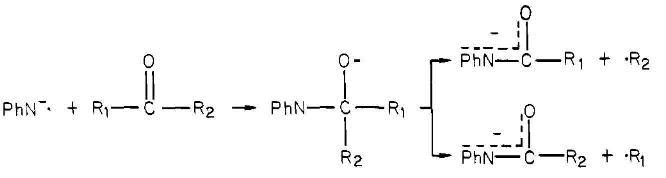
Table I. Summary of Kinetic and Product Data for the Ion–Molecule Reaction of $PhN^{-}\cdot$ with Certain Carbonyl Compounds

ion + neutral reactants		products [assumed neutral]	fraction of product ion signal[c]	k_{total},[a] cm^3 $molecule^{-1}$ s^{-1}
$PhN^{-}\cdot + CH_3CHO$	→	$PhNCOCH_3^-$ [+ ·H]	0.59	$(8.1 \pm 0.4) \times 10^{-11}$
	→	$PhNCHO^-$ [+ $\cdot CH_3$]	0.31	
	→	H_2CCHO^- [+ PhNH·]	0.10[b]	
$PhN^{-}\cdot + CH_3COCH_3$	→	$PhNCOCH_3^-$ [+ $\cdot CH_3$]	0.81	$(6.4 \pm 0.4) \times 10^{-12}$
	→	$CH_2COCH_3^-$ [+ PhNH·]	0.19[b]	
$PhN^{-}\cdot + CF_3COCF_3$	→	$PhNCOCF_3^-$ [+ $\cdot CF_3$]	1.00	$(4.9 \pm 0.1) \times 10^{-10}$
$PhN^{-}\cdot + CF_3COCH_3$	→	$PhNCOCF_3^-$ [+ $\cdot CH_3$]	0.36	$(9.1 \pm 0.6) \times 10^{-10}$
	→	$PhNCOCH_3^-$ [+ $\cdot CF_3$]	0.15	
	→	$CF_3COCH_2^-$ [+ PhNH·]	0.49	
$PhN^{-}\cdot + CH_3COCOCH_3$	→	$PhNCOCH_3^-$ [+ CO + $\cdot CH_3$]	0.98	$(6.4 \pm 0.5) \times 10^{-10}$
	→	$CH_2COCOCH_3^-$ [+ PhNH·]	0.02	
$PhN^{-}\cdot$ + cyclobutanone	→	$PhNCOCH_2^{-}\cdot$ [+ $H_2C{=}CH_2$]	0.96	$(6.9 \pm 0.3) \times 10^{-11}$
	→	 [+ PhNH·]	0.04	
$PhN^{-}\cdot + CF_3CO_2CH_3$	→	$PhNCOCF_3^-$ [+ $\cdot OCH_3$]	0.99	$(9.1 \pm 0.3) \times 10^{-10}$
	→	$PhNCO_2CH_3^-$ [+ $\cdot CF_3$]	0.01	
$PhN^{-}\cdot + CH_3CO_2CH_3$	→	$PhNCOCH_3^-$ [+ $\cdot OCH_3$]	0.88	1.5×10^{-13} [d]
	→	$CH_2CO_2CH_3^-$ [+ PhNH·]	0.12	

[a] k's are estimated to be accurate to ±30%. Errors given are deviations from multiple determinations. When the flowing afterglow apparatus conditions were changed to $\bar{v} = 50$ m s^{-1} and $P_{He} = 1.2$ torr, no changes in k or primary product ion distributions were observed. [b] This product channel includes a small contribution of further condensation of the enolate anion with the neutral carbonyl compound. [c] Not corrected for mass discrimination. [d] Determined at $P_{He} = 1.1$ torr, $\bar{v} = 50$ m s^{-1}.

The use of $PhN^{-}\cdot$ as a mechanism probe offers a distinct advantage over the use of closed-shell anions in such studies, because the addition adduct is an anion radical which has a low threshold radical β-fragmentation pathway. Such fragmentation yields the (M–R) adducts (eq 1) retaining the R—C═O acyl portions of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(1)

the original carbonyl compound. The relative amounts of the $PhNCOR_1^-$ and $PhNCOR_2^-$ product ions depend on the bond dissociation energies [$D(C{-}R_1)$ and $D(C{-}R_2)$] in the adduct **1**, assuming that the addition adducts are at thermal energies.

$PhN^{-}\cdot$ was produced in our flowing afterglow apparatus (usual conditions: helium buffer gas, $P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}, 298 K) by dissociative electron attachment to phenyl azide.[5] The neutral carbonyl compounds were added to the flow downstream of the ion preparation-thermalization region. The relative concentrations of $PhN^{-}\cdot$ and the anion products of the ion-molecule reactions were monitored with a quadrupole mass spectrometer. The decay of the $PhN^{-}\cdot$ ion signal was strictly exponential for more than an order of magnitude range of carbonyl compound concentration added to the flow.

Table II. Gas-Phase Relative Rate Constants for the Addition Reactions of $PhN^{-}\cdot$ with Carbonyl Compounds[a]

compd	$k_{rel}^{C=O}$
CH_3COCH_3	1
CH_3CHO	14
CF_3COCF_3	95
CF_3COCH_3	88
$CH_3COCOCH_3$	122[b]
cyclobutanone	13
$CF_3CO_2CH_3$	176
$CH_3CO_2CH_3$	0.03

[a] These relative rate constants are k_{total} × (sum of the fractions of those channels yielding acyl anilide anions) from Table I. [b] If the symmetry factor is used, the $k_{rel}^{C=O} = 61$ for biacetyl.

The total rate constants and branching channels for the reactions of $PhN^{-}\cdot$ with the carbonyl compounds studied are listed in Table I. In two cases, CH_3COCH_3 and CF_3COCF_3, minor (1–3%) product ion signals (m/z 149 and 257, respectively) attributed to the addition adducts **1** were observed. Production of acylanilide anions was the major process observed, accompanied by varying amounts of proton transfer depending on the acidity of the carbonyl compound.

The $k_{rel}^{C=O}$ values listed in Table II involve only those reaction channels yielding acylanilide anions formed by carbonyl addition/fragmentation. Several interesting points emerge from these $k_{rel}^{C=O}$ values: (a) all of the rate constants are below the Langevin or ADO limits for ion–molecule collisions;[8] (b) a range of almost 6000 in $k_{rel}^{C=O}$ is observed; (c) in most respects, the relative reactivities of these carbonyl reactants with $PhN^{-}\cdot$ in the gas phase are those observed or expected for nucleophilic additions in solution; (d) additivity for the substituent effect of the CF_3 group is absent; and (e) the addition/fragmentation process observed with the alicyclic cyclobutanone generates an interesting, new type of anion radical **2** for future studies (eq 2).[9]

The large range in $k_{rel}^{C=O}$ observed in Table II is unusual in such a series of gas-phase ion–molecule reactions.[10] Assuming the common mechanism of nucleophilic attack by $PhN^{-}\cdot$ in these reactions, a barrier in the addition process is required. Since small,

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(4) (a) Based on the nucleophilicity order (Bohme et al.[4c]) of nucleophiles in their reactions with the methyl halides, $PhN^{-}\cdot$ must be considered to be a poor nucleophile toward saturated carbon: $PhN^{-}\cdot + CH_3Br \rightarrow Br^-$ [+ $PhNCH_3\cdot$] ($k = (1.8 \pm 0.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) and $PhN^{-}\cdot + CH_3Cl \rightarrow Cl^-$ [+ $PhNCH_3\cdot$] ($k = 1.7 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}).[4b] This is expected for a π-delocalized anion in $PhN^{-}\cdot$.[5] (b) McDonald, R. N.; Chowdhury, A. K., unpublished results. (c) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.

(5) The structure of the anion m/z 91 formed from $PhN_3 + e^-$ is considered to be $PhN^{-}\cdot$ since (1) all bonding and nonbonding orbitals are occupied, (2) its thermochemical properties[6] do not agree with those expected for isomeric species, and (3) the temperature and method of generation of this ion radical would not allow for endothermic rearrangements. The electronic configuration of $PhN^{-}\cdot$ is believed to be that of triplet PhN with the out-of-plane $3b_2$ orbital doubly occupied.[7]

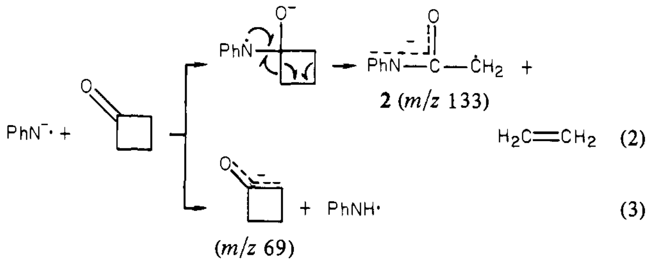
(6) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 5118.

(7) (a) Reiser, A.; Bowes, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162. (b) Berry, R. S. In "Nitrenes"; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; Chapter 2.

(8) Su, T.; Bowers, M. T. *Gas Phase Ion Chem.* **1979**, *1*, Chapter 3.

(9) Formation of the ion radical m/z 133 by addition/fragmentation of $PhN^{-}\cdot$ to this four-membered ring ketone is probably a function of the strain energy in this ketone.

(10) For example, see: Talrose, V. L.; Vinogradov, Karin, I. K. *Gas Phase Ion Chem.* **1979**, *1*, Chapter 8.



2 (*m/z* 133)

(*m/z* 69)

but discernible, ion signals for addition adducts **1** were observed for a slow (CH_3COCH_3) and a fast (CF_3COCF_3) reactant, it is reasonable to assume that these adducts are tetrahedral anion radicals rather than loss complexes[2] and that these addition/fragmentation reactions proceed via such an intermediate.[2,3,11,12]

The fragmentation products from the acyclic carbonyl compounds studied establish the following group fragmentation order for adduct **1**: $CH_3O \sim CH_3CO > H > CH_3 > CF_3$. From our previous report of the reactions of $PhN^{-}\cdot$ with methyl vinyl ketone, we found $CH_3 > CH_2{=}CH$ fragmentation from the 1,2-addition adduct.[1] This fragmentation order appears to largely reflect the expected stabilities of the acylanilide anionic products.[13]

Part of our present studies involves developing the related chemistry of other molecular and atomic hypovalent anion radicals. It is hoped that these results, especially of the atomic species, will better lend themselves to theoretical calculations of the potential surfaces for these reactions.

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[11] Brauman et al.[2a] favor a double-minimum well model for the reactions of acid halides with nucleophiles.

[12] (a) A theoretical study (ab initio) for addition of HO^- to the carbonyl group of formamide indicated no barrier to addition: Alagona, G.; Scrocco, E.; Tomasi, J. *J. Am. Chem. Soc.* **1975**, *97*, 6976. (b) A triple-minimum potential surface appears to be required to explain our data for these addition/fragmentation reactions.

[13] R. N. McDonald and A. K. Chowdhury (unpublished results) have found $PA(PhNCOCH{=}CH_2^-) \leq 345$ kcal mol^{-1} compared to $PA(PhNCOCH_3^-) = 358 \pm 2$ kcal mol^{-1} (Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1) (PA = proton affinity).

Gas-Phase Ion-Molecule Reactions of Phenylnitrene Anion

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The recent report[1] of the production of phenylnitrene anion, $PhN^{-}\cdot$, in a flowing afterglow and its subsequent reactions with PhN_3 prompts us to communicate some preliminary results of our independent investigations into the chemistry of this interesting species. We have found it possible to generate and trap $PhN^{-}\cdot$ from electron impact on PhN_3 at low pressure ($<10^{-7}$ torr) in a pulsed ion cyclotron resonance (ICR) spectrometer. Nitrene anion formation from azides under our conditions appears to be a general phenomenon, as trimethylsilyl azide[2] and ethyl azide[3] also produce the corresponding nitrene anions upon electron impact. We report here some unusual bimolecular reactions involving $PhN^{-}\cdot$ which have no precedent in ion-molecule chemistry.

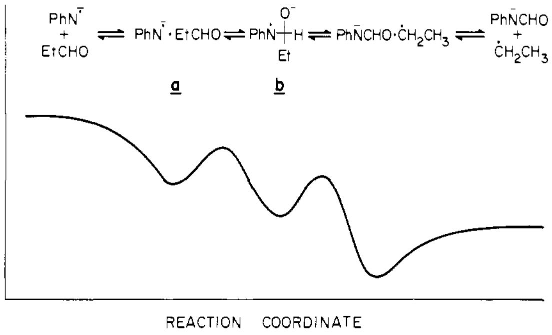

Figure 1. Proposed potential-energy-reaction coordinate diagram for the major pathway in reaction 1. The relative heights of the minima are based on rough thermochemical estimates.

Using the acidity bracketing technique,[4] we place the proton affinity (PA) of $PhN^{-}\cdot$ between those of $t\text{-}BuO^-$ and $PhCH_2O^-$; thus we obtain $PA(PhN^{-}\cdot) = 371 \pm 3$ kcal/mol, in good agreement with the previous value.[1a] However, in the presence of CH_3CH_2CHO, which is 3.7 kcal/mol more acidic[4] than $PhCH_2OH$, no (<5%) proton abstraction by $PhN^{-}\cdot$ is seen. Instead, two fairly slow reactions ($k_{1a} + k_{1b} = 7.0 \pm 0.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) produce anions with *m/e* 120 (1a, ~75%) and 148 (1b, ~25%). We believe these reactions to proceed as shown in reaction 1.

$$PhN^{-}\cdot + CH_3CH_2CHO \nrightarrow Ph\dot{N}H + CH_3\bar{C}HCHO \qquad \Delta H° = -6 \text{ kcal/mol}$$
$$\xrightarrow{k_{1a}} Ph\bar{N}CHO + CH_3CH_2\cdot \qquad \Delta H° = -17 \text{ kcal/mol}$$
$$\xrightarrow{k_{1b}} Ph\bar{N}COCH_2CH_3 + H\cdot \qquad \Delta H° = -9 \text{ kcal/mol} \quad (1)$$

Reaction of $PhN^{-}\cdot$ with CH_3CHO produces $Ph\bar{N}CHO$ and $Ph\bar{N}COCH_3$ and again gives no enolate. (Proton transfer here is 5 kcal/mol exothermic.) In this case, however, the H-atom displacement is the major pathway, in contrast to the reaction with propionaldehyde. With the substantially more acidic CH_3COCF_3, the major reaction channel (~80%) is rapid proton transfer; a minor product (~20%) is *m/e* 188, which we believe is $Ph\bar{N}COCF_3$ (reaction 2).

$$PhN^{-}\cdot + CH_3COCF_3 \xrightarrow{a} Ph\dot{N}H + \bar{C}H_2COCF_3 \qquad \Delta H° = -22 \text{ kcal/mol}$$
$$\xrightarrow{b} Ph\bar{N}COCF_3 + CH_3\cdot \qquad \Delta H° = -30 \text{ kcal/mol} \quad (2)$$

Although *N*-alkylation of $PhN^{-}\cdot$ is strongly exothermic, reactions with CH_3Br and $CF_3CO_2\,CH_3$ do not proceed with appreciable velocity through the commonly observed[5] S_N2 reaction channels. We observe only slow reaction (reaction 3) with CH_3Br ($k_3 = 1.9 \pm 0.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), while with $CF_3CO_2CH_3$ a rapid reaction ($k_4 = 6.2 \pm 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) produces $Ph\bar{N}COCF_3$ as the only detectable product (reaction 4).

$$PhN^{-}\cdot + CH_3Br \rightarrow Ph\bar{N}CH_3 + Br^- \qquad \Delta H° = -48 \text{ kcal/mol} \quad (3)$$

Occurrence of proton transfer (reaction 2) and radical displacement (reaction 1) pathways show that $PhN^{-}\cdot$ can exhibit both free-radical and anionic behavior; to the extent that a single Lewis structure suffices, it may be described by a structure in which the negative charge is delocalized into the phenyl ring and the odd

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[†] National Science Foundation Fellow, 1977-1980.

[1] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1980**, *102* 5118. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. "Abstracts", Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug 17-22, 1980, p 51.

[2] Jackson, R. L.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.*, in press. However, the chemistry of (trimethylsilyl)nitrene anion is not conveniently studied due to a rapid reaction with the parent azide to produce N_3^-.

[3] Rynard, C. M., unpublished results.

[4] Bartmess, J. E.; McIver, R. T. *Gas Phase Ion Chem.* **1979**, *2*, Chapter 11.

[5] Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219.

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