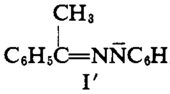
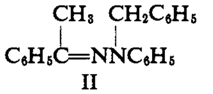
1,4-Dianions of Phenylhydrazones Having an α-Hydrogen[1]

Sir:

Acetophenone phenylhydrazone has recently been converted to the monoanion I′ by 1 equiv of potassium amide in liquid ammonia, as evidenced by N-benzylation with benzyl chloride to form II.[2]

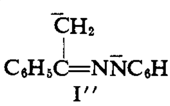

$C_6H_5\overset{CH_3}{C}{=}N\bar{N}C_6H_5$

I′

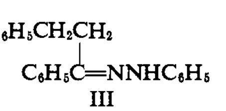

$C_6H_5\overset{CH_3}{C}{=}N\overset{CH_2C_6H_5}{N}C_6H_5$

II

This phenylhydrazone has now been converted to the dianion I″ by 2 equiv of the alkali amide in liquid ammonia, as evidenced by preferential C-benzylation with 1 equiv of benzyl chloride to afford III, which was independently synthesized from benzylacetophenone and phenylhydrazine.


$C_6H_5\overset{\bar{C}H_2}{C}{=}N\bar{N}C_6H_5$

I″

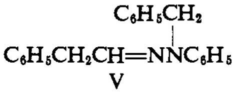

$C_6H_5\overset{C_6H_5CH_2CH_2}{C}{=}NNHC_6H_5$

III

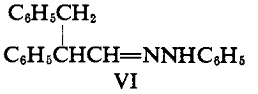
Similarly, phenylacetaldehyde phenylhydrazone was N-benzylated through its monoanion and C-benzylated through its dianion IV″ to form V and VI, respectively. Also, dianion IV″ underwent dibenzylation with 2 equiv of benzyl chloride to give VII.

$C_6H_5\bar{C}HCH{=}N\bar{N}C_6H_5$

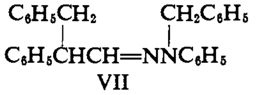
IV″


$C_6H_5CH_2CH{=}N\overset{C_6H_5CH_2}{N}C_6H_5$

V

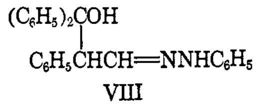

$C_6H_5\overset{C_6H_5CH_2}{C}HCH{=}NNHC_6H_5$

VI

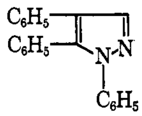

$C_6H_5\overset{C_6H_5CH_2}{C}HCH{=}N\overset{CH_2C_6H_5}{N}C_6H_5$

VII

Likewise, dianion IV″ underwent an addition reaction with benzophenone and benzoylation, accompanied by cyclization with methyl benzoate, to afford VIII and IX, respectively.


$C_6H_5\overset{(C_6H_5)_2COH}{C}HCH{=}NNHC_6H_5$

VIII


IX

The yields of all of these products were good (50–76%). The structures of the new compounds III, V, VI, VII, and VIII were supported by analyses and infrared and nmr spectra. Cyclic structure IX was supported by infrared and by essential agreement of melting point with the values reported previously.[3] The present method not only affords a better yield but also appears more convenient.

These results represent a significant advance in our studies of dianions, the two anionic portions of which are in resonance.[4] Dianions I″ and IV″ are to be distinguished from ordinary 1,4-dianions in which the two anionic portions are not in resonance. Because the carbanion portion of I″ or IV″ is much more nucleophilic, C-condensations can be effected to the apparent exclusion of N-condensations. However, C- and N-condensations might be realized to form cyclic products with appropriate electrophilic compounds.

Work is in progress on condensations of dianions I″ and IV″ with other electrophilic compounds and on similar studies with various other phenylhydrazones including osazones and related compounds.

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(1) Supported by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

(2) W. G. Kenyon and C. R. Hauser, *J. Org. Chem.*, **30**, 292 (1965).

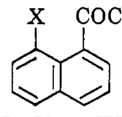
(3) W. Wislicenus and A. Ruthing, *Ann.*, **379**, 229 (1911); J. Matti and M. Perrier, *Bull. Soc. Chim. France*, **22**, 525 (1955); H. O. House and D. Ryerson, *J. Am. Chem. Soc.*, **83**, 979 (1961).

(4) Several 1,3-dianions, such as that of acetylacetone, have previously been prepared; see C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

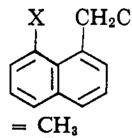
Relative Contributions of Hyperconjugation and Nonbonded Interactions to Secondary Isotope Effects

Sir:

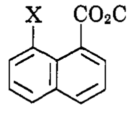
Solvolytic rate constants and isotope effects for compounds I–III[1] are summarized in Table I. The absence of formal hyperconjugative structures involving the isotopically labeled group X dictated the study of these compounds as a probe into the still debated question of the relative contributions of hyperconjugation and nonbonded interactions to secondary isotope effects.



Ia, $X = CH_3$
b, $X = CD_3$
c, $X = H$
d, $X = D$



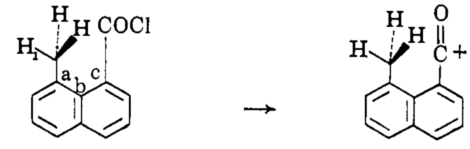
IIa, $X = CH_3$
b, $X = CD_3$
b′, $(-CD_2Cl, X = CH_3)$
c, $X = H$
d, $X = D$
d′, $(-CD_2Cl), X = H$



IIIa, $X = CH_3$
c, $X = H$
d, $X = D$

Since k_{Ia}/k_{Ic} is about 10, whereas the nucleophilic k_{IIIa}/k_{IIIc} is less than 10^{-3}, Ia must solvolyze by a limiting mechanism. As judged from k_{IIa}/k_{IIc} of about 30 and an α-isotope effect $k_{IIa}/k_{IIb'}$ of 1.32, IIa also solvolyzes by a limiting mechanism. That in formic acid IIc solvolyzes by a limiting mechanism has been established[2] and supported here by the α-isotope effect $k_{IIc}/k_{IId'}$ of 1.35.

From currently available potential functions,[3,4] $V(r)$, and using Bartell's procedure,[3] we have calculated and summarized in Table II the nonbonded isotope effect (k_{Ia}/k_{Ib}) for IV → V as a function of the dihedral



IV

V

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(1) Isotopic purity for d_1 compounds: 98% d_1, 2% d_0; for d_3 compounds: 97.3% d_3, 2.7% d_2. We thank S. Meyerson of the American Oil Co., Whiting, Ind., for the mass spectral analyses.

(2) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946 (1957).

(3) L. S. Bartell, *J. Am. Chem. Soc.*, **83**, 3567 (1961).

(4) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965). For the H ↔ C interaction the function given by J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961), was used.