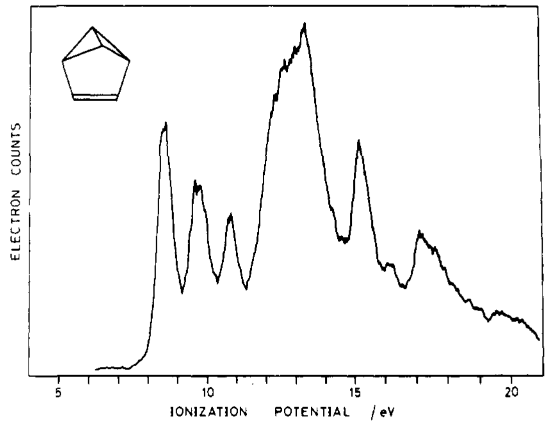


Figure 1. He I photoelectron spectrum of benzvalene.

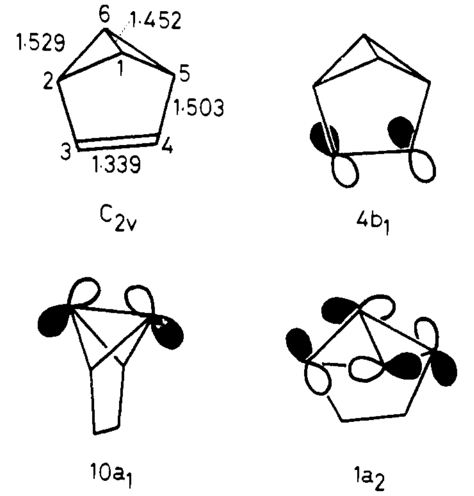


Figure 2. Benzvalene geometry and uppermost occupied molecular orbitals from SPINDO calculation.

Table I. Assignment of Experimental and Calculated Vertical Ionization Potentials for Benzvalene (in eV)

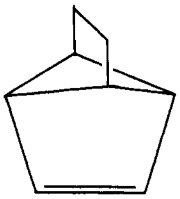
MO	Exptl[a]	Ab initio[b] (-0.9ϵ)	SPINDO[c] $(-\epsilon)$
$4b_1$	8.54	7.8	9.59
$10a_1$	9.60	9.2	10.16
$1a_2$	10.69	10.3	10.57
$6b_2$	12.3	11.9	12.30
$3b_1$	12.7	12.6	12.11
$5b_2$	13.0	12.8	12.48
$9a_1$	13.2	12.9	13.31
$8a_1$	15.1	15.4	14.80

[a] Accuracies vary between ±0.04 and ±0.1 eV. [b] Reference 5. [c] This work.

is noteworthy that the first ionization potential is intermediate in value to those predicted by the ab initio and SPINDO calculations. Otherwise the pattern of photoelectron bands correlates well with both sets of calculated results, which agree except for the order of $3b_1$ and $6b_2$.

The composition of the molecular orbitals associated with the first three bands, as indicated by the SPINDO calculation, are illustrated in Figure 2 together with the benzvalene geometry. The first band is, as expected, related to the π-type $4b_1$ MO of the C_3–C_4 double bond. However, the observation that the band is broad and unstructured indicates that the MO is composed of reasonable contributions from other atoms. The second level is associated with the short bridging C_1–C_6 bond, and relates to an approximate σ-type MO of a_1 symmetry. The third band is involved with the four-center MO of a_2 symmetry.

The low first vertical IP of benzvalene leads us to suspect that the unusual electronic absorption spectrum of benzvalene ($\lambda_{\max}$ 217 nm)[8] is interpretable in terms of a valence shell transition (either $\pi^* \leftarrow \pi$ (b_1) or $\pi^* \leftarrow \sigma$ (a_1)) upon which is superimposed the first member of a low lying Rydberg series (ns $\leftarrow \pi$ or ns $\leftarrow \sigma$). To support this argument we note that the quantum defect of 0.89 is strikingly similar to that observed for tricyclo[3.3.0.0^{2,6}]oct-3-ene of 0.90, where the Rydberg nature of the absorption spectrum ($\lambda_{\max}$ 218 nm) is well confirmed.[9,10]



References and Notes

(1) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).
(2) G. Bieri, E. Heilbronner, M. J. Goldstein, R. S. Leight, and M. S. Lipton, *Tetrahedron Lett.*, 581 (1975).
(3) T. J. Katz, E. J. Wang, and N. Acton, *J. Am. Chem. Soc.*, **93**, 3782 (1971).
(4) R. G. Dromey and J. B. Peel, *Aust. J. Chem.*, **28**, 2353 (1975).
(5) M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Am. Chem. Soc.*, **96**, 17 (1974).
(6) E. Lindholm, C. Fridh, and L. Asbrink, *Discuss. Faraday Soc.*, **54**, 127 (1972).
(7) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **94**, 5915 (1972); **95**, 4506 (1973).
(8) D. W. T. Griffith, J. E. Kent, and M. F. O'Dwyer, *J. Mol. Spectrosc.*, **58**, 427 (1975).
(9) B. M. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).
(10) P. Bischof, R. Gleiter, M. J. Kukla, and L. A. Paquette, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 177 (1974).

P. J. Harman, J. E. Kent
Department of Chemistry, Monash University
Clayton, Victoria, Australia, 3168

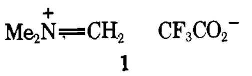
T. H. Gan, J. B. Peel,* G. D. Willett
Department of Physical Chemistry, La Trobe University
Bundoora, Victoria, Australia, 3083

Received September 8, 1976

New Applications of the Mannich Reaction. Use of Dimethyl(methylene)ammonium Trifluoroacetate for Regiospecific Carbanion Quenching. A New Route to α-Methylene-γ-butyrolactone

Sir:

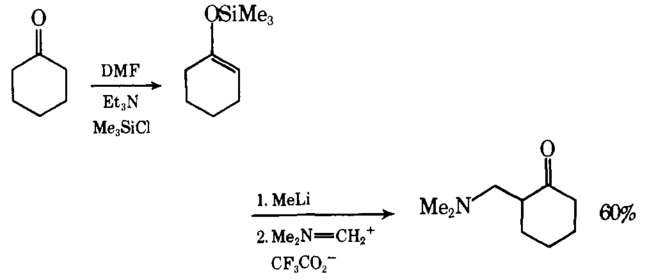
A new approach to the Mannich reaction has been discovered which permits regiospecific alkylation and convenient derivatization of ketones, esters, and carboxylic acids. This approach employs dimethyl(methylene)ammonium trifluoroacetate, **1**, one of several related Mannich reagents which have become available in the past several years.[1] Our Mannich approach essentially involves trapping pregenerated "carbanions". Because **1** may be utilized in aprotic solvents, this scheme permits an uncoupling of Mannich reactivity from the usual requirement of acidity in a protic solvent. The approach is entirely analogous to carbanion trapping with formaldehyde, a method introduced by Grieco[2] some years ago and more recently applied by Stork[3] to regiospecifically generated anions. Potential advantages of the Mannich approach are less dialkylation, polymerization, and greater product stability.



$Me_2\overset{+}{N}{=}CH_2\quad CF_3CO_2^-$

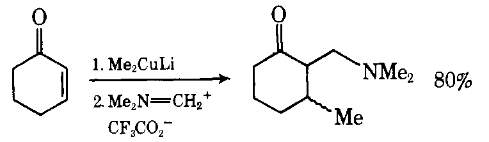
1

Very recently Danishefsky[4] published a Mannich technique involving addition of dimethyl(methylene)ammonium iodide to silyl enol ethers or enolates. Mannich products were formed regiospecifically and in high yield. Working independently, and using a slightly different approach, our data indicates similar results. Our reactions involved cleavage of the silyl enol ether[5] with methyllithium, followed by addition of dimethyl(methylene)ammonium trifluoroacetate. Thus the silyl enol ether of cyclohexanone in THF was cooled in a dry ice bath and a 10% molar excess of methyllithium was added. After 0.5 h, the Mannich reagent[6] was added (10% molar excess), the bath was removed, and the solution permitted to warm to room temperature. Water was then added, the pH adjusted to 10, and the products were isolated by extraction and purified by vacuum distillation.



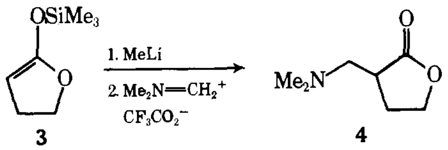
To determine whether regiospecific dimethylaminomethylation was possible, silyl enol ethers of unsymmetrical ketones were generated using conditions favoring the thermodynamic or kinetic product; these were then treated as above. The product distributions demonstrate the reaction to be regiospecific. Minor processes involving isomerization and disubstitution cannot be entirely discounted, but these were undetected in our rather small (ca. 1 g) samples. Isomerization is not anticipated to be a major problem in view of the rapidity of the reaction.

The trapping technique appears to be quite general. Treatment of 2-cyclohexen-1-one with lithium dimethylcyprate, followed by addition of the immonium reagent, resulted in **2**.



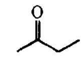
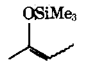
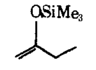
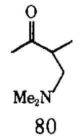
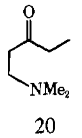
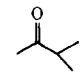
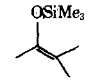
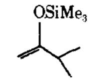
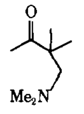
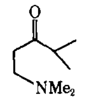
2

We sought to extend this synthetic scheme to the generation of α-methylene-γ-butyrolactone. The synthesis of this unit has received considerable attention[7] because of its presence in several compounds displaying attractive cytotoxic activity.[8] Unactivated esters are not responsive to the classic Mannich conditions and the usual activation routes typically involve modest yield reactions.[9] The silyl enol ethers of ketones and esters, including that of γ-butyrolactone,[10] are generally formed in high yield. Treatment of **3** with methyllithium, followed by quenching with dimethyl(methylene)ammonium trifluoroacetate, resulted in a 63% yield of the Mannich product.[11] Conversion of **4** to α-methylene-γ-butyrolactone is a well-established, essentially quantitative procedure involving treatment of the amine with methyl iodide and then aqueous sodium bicarbonate.



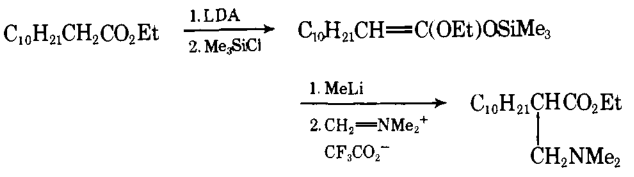
3 4

Table I. Mannich Alkylation of Ketones Using Dimethyl(methylene)ammonium Trifluoroacetate

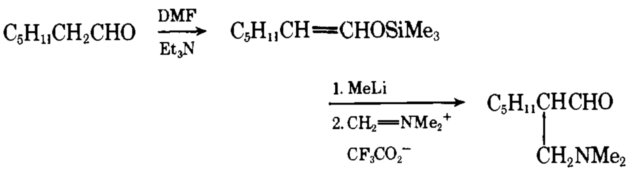
Ketone	Silyl ether[a]		Mannich product[b]		Yield
					
A[c]	81	19	80	20	50
B[d]	48	52	48	52	53
					
A[c]	61	39	61	39	61
B[d]	20	80	20	80	65

[a] Isomeric distribution determined by GLC. [b] Isomeric distribution determined by ¹H NMR, accurate to ±5%. [c] Procedure A, ref 5a. [d] Procedure B, ref 5a.

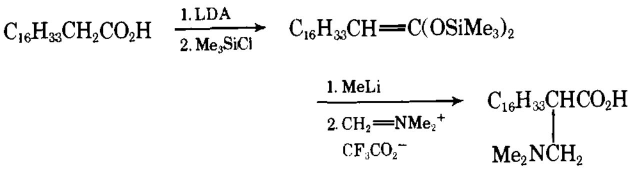
As further preliminary indication of the generality of the reaction, a 50% overall yield of the Mannich product was obtained from ethyl laurate; an overall yield of 30% was isolated from heptanal; the yield was 45% from stearic acid.



$$C_{10}H_{21}CH_2CO_2Et \xrightarrow[2.\ Me_3SiCl]{1.\ LDA} C_{10}H_{21}CH{=}C(OEt)OSiMe_3 \xrightarrow[2.\ CH_2{=}NMe_2^+\ CF_3CO_2^-]{1.\ MeLi} C_{10}H_{21}\underset{CH_2NMe_2}{\underset{|}{C}}HCO_2Et$$



$$C_5H_{11}CH_2CHO \xrightarrow[Et_3N]{DMF} C_5H_{11}CH{=}CHOSiMe_3 \xrightarrow[2.\ CH_2{=}NMe_2^+\ CF_3CO_2^-]{1.\ MeLi} C_5H_{11}\underset{CH_2NMe_2}{\underset{|}{C}}HCHO$$



$$C_{16}H_{33}CH_2CO_2H \xrightarrow[2.\ Me_3SiCl]{1.\ LDA} C_{16}H_{33}CH{=}C(OSiMe_3)_2 \xrightarrow[2.\ CH_2{=}NMe_2^+\ CF_3CO_2^-]{1.\ MeLi} C_{16}H_{33}\underset{Me_2NCH_2}{\underset{|}{C}}HCO_2H$$

The present route is attractive because of its mildness, relative simplicity, and reasonable yields. It provides a further example of the use of regiospecific enolates derived from silyl enol ethers. We have also been investigating the approach published by Danishefsky in which the use of methyllithium is avoided. Using dimethyl(methylene)ammonium chloride,[1c] we have found the yields of Mannich products to be improved and very similar to those reported by Danishefsky.

References and Notes

(1) (a) A. Ahond, A. Cavé, C. Kan-Fan, and P. Potier, *Bull. Soc. Chim. Fr.*, 2707 (1970); (b) J. Schreiber, H. Maag, N. Hashimoto, and A. Eschenmoser, *Angew. Chem., Int. Ed. Engl.*, **10**, 330 (1971); Y. Jasor, M. L. Luche, and M. Marguet, *J. Chem. Soc., Chem. Commun.*, 253 (1974); P. Binger and R. Koster, *Chem. Ber.*, **108**, 395 (1975); A. Ahond, A. Cavé, C. Kan-Fan, H. P. Husson, J. de Rostolan, and P. Potier, *J. Am. Chem. Soc.*, **90**, 5622 (1968); (c) H. Böhme, M. Hilp, L. Koch, and E. Ritter, *Chem. Ber.* **104**, 2018 (1971).

(2) P. A. Grieco and K. Hiroi, *J. Chem. Soc., Chem. Commun.*, 1317 (1972); P. A. Grieco, M. Nishizawa, S. D. Burke, and N. Marinovic, *J. Am. Chem. Soc.*, **98**, 1612 (1976).

(3) G. Stork and J. D'Angelo, *J. Am. Chem. Soc.*, **96**, 7114 (1974).

(4) S. Danishefsky, T. Kitahara, R. McKee, and P. Schuda, *J. Am. Chem. Soc.*, **98**, 6715 (1976).

(5) Silyl enol ethers of ketones were prepared according to the procedure of: (a) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969). (b) See also: G. Stork and P. F. Hudrik, *J. Am. Chem. Soc.*,

90, 4462, 4464 (1968). The ethers of esters were prepared as in: C. Ainsworth, F. Chem, and Y.-N. Kuo, *J. Organomet. Chem.*, **46**, 59 (1972). The ketene bis(trimethylsilyl)acetal of stearic acid was prepared according to: C. Ainsworth and Y.-N. Kuo, *Ibid.*, **46**, 73 (1972).

(6) Prepared according to ref 1a except that for good yields dimethyl(methylene)ammonium trifluoroacetate must be distilled before use in carbanion quenching experiments (bp 130–140 °C (0.05 mm)).

(7) Only recent reviews are listed: R. B. Hammill, C. A. Wilson, and T. A. Bryson, *Synth. Commun.*, **5**, 245 (1975); P. A. Grieco, *Synthesis*, 67 (1975).

(8) S. M. Kupchan, M. Eakin, and A. Thomas, *J. Med. Chem.*, **14**, 1147 (1971); S. M. Kupchan, *Trans. N.Y. Acad. Sci.*, **32**, 85 (1970); K. Lee, E. Haung, C. Piantadosi, J. Pagano, and T. Greissman, *Cancer Res.*, **31**, 1649 (1971); W. Herz, G. Hogenauer, and A. de Vivai, *J. Org. Chem.*, **29**, 1700 (1964); S. M. Kupchan, R. Hemingway, D. Werner, and A. Karim, *ibid.*, **34**, 3903, 3908, (1969).

(9) See ref 7 for discussion of activation.

(10) J. K. Rasmussen and A. Hassner, *J. Org. Chem.*, **39**, 2558 (1974). In our hands the yield was fairly modest (40%), and the products of C-silylation and Claisen condensation were observed. It appears that the O-ether can be prepared in good yield only on a small scale.

(11) The IR, ^{1}H NMR, refractive index, and boiling point were consistent with those reported by C. R. Hutchinson, *J. Org. Chem.*, **39**, 1854 (1974). The melting point of the methyl iodide derivative was 217–218 °C, or somewhat higher than the melting points between 200 and 207 °C reported in the Hutchinson paper.

Norman L. Holy,* Yu Fang Wang
Department of Chemistry, Western Kentucky University
Bowling Green, Kentucky 42101

Received August 24, 1976

An ab Initio Model for the Quenching of Ketone Phosphorescence by Amines

Sir:

The quenching of fluorescence and phosphorescence of ketones by electron donors such as amines has been attributed to a charge transfer interaction.[1] The sensitivity of this reaction to steric effects[2] implies that quenching requires close approach of the amine and ketone. Some have invoked transient, stable excited complexes (exciplexes) as obligate intermediates,[1,3] though formation of exciplexes in the *gas phase* quenching of ketone emission by amines has been questioned.[4] If one assumes that the exciplex can be approximated by the zero-order charge transfer state, one predicts a stable exciplex for triplet acetone and triethylamine, $\Delta G_{ex} \sim -16$ kcal/mol.[5] For triplet formaldehyde and ammonia, however, the exciplex energy is estimated to be 66 kcal/mol higher in energy than the isolated $CH_2{=}O^{*3}$.

One way of gaining insight into the quenching process is to use ab initio calculations to examine features of the hypersurface of two interacting molecules. Given a suitable model for the interacting species and a modest basis set, fairly large regions of the hypersurface can be searched and interesting geometries can be optimized. This approach is very useful to the organic photochemist who wishes broad insights into the general features of the interaction, but who does not have access to a vast computer budget.

We have investigated the interaction of ammonia and formaldehyde in the lowest singlet (ground) and triplet states using ab initio calculations at the STO-3G level without configuration interaction.[6] This system is the simplest model for the quenching of ketone phosphorescence by amines. We focussed on the "head-on" interaction in which ammonia approached the oxygen of formaldehyde. This seemed a reasonable place to begin our search of the hypersurface, since in this geometry NH_3 can donate electrons into the hole produced upon excitation of CH_2O to its $n\pi^*$ triplet state.[3] It quickly became evident that strong destabilization occurred in the ground state singlet at $r_{(NO)}$ distances more remote than in the corresponding triplet. This pointed to a readily accessible surface crossing[10] which could provide a quenching mechanism. This paper describes a region of the hyperspace where those surfaces cross.

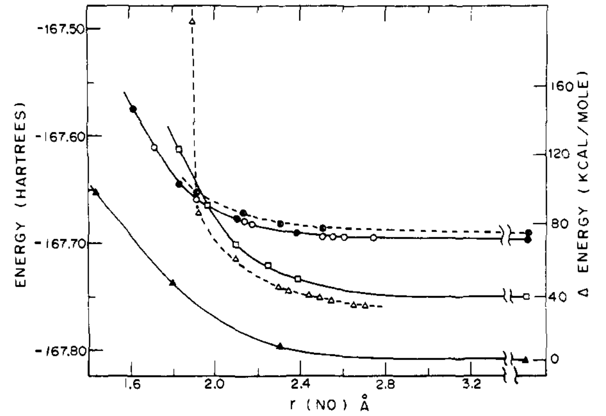
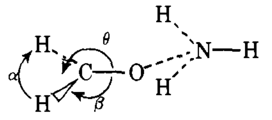
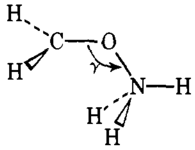


Figure 1. Plot of energy (in hartrees) vs. $r_{(NO)}$ for the approach of NH_3 to the oxygen of CH_2O in the ground state and lowest triplet state as determined by ab initio calculations (STO-3G). Several cross sections are shown. Solid symbols represent fully optimized geometries. The lowermost line represents the ground state in approach II. Other lines describe approach I. See text. The following symbols represent the lowest energy triplet state approach (-○-), its planar (C_S) distortion (- - -●- - -), the same geometries in the ground state (—□—), and its planar distortion (- - -△- - -), respectively.

We investigated two approaches of CH_2O and NH_3. The in-plane approach I becomes distorted from C_s symmetry as the two CH bonds are bent out of the plane originally defined by planar formaldehyde. The perpendicular approach II maintains C_s symmetry even when these CH bonds are bent.



I



II

Geometries of NH_3 and ground state and triplet formaldehyde were fully optimized. In the supermolecules, those CH and NH bond lengths were fixed, as was the $\widehat{ONH}$ pyramidal angle. For simplicity we assumed that the $\widehat{HCH}$ angle (α) equalled the $\widehat{HCO}$ angle (β). This allowed these angles and the pyramidal angle (θ) at carbon to be optimized via a single parameter. Other modes were fully optimized, often iteratively. The algorithm used was to optimize $r_{(CO)}$, the pyramidal angle θ, and then $\widehat{CON}$, for arbitrarily chosen $r_{(NO)}$ values. The closed symbols in Figure 1 represent geometries optimized in this manner. Calculations without configuration interaction give no indication of the correlation energy. Since they do give good relative energies, the triplet manifold was arbitrarily adjusted so that the isolated optimized formaldehyde triplet lay 72 kcal/mol[11] above the optimized ground state.

Figure 1 shows several cross-sections through the hyperspace resulting from the $CH_2O{\cdots}NH_3$ interaction. The lowermost line, for the perpendicular approach II, represents the lowest energy approach of NH_3 to the oxygen of ground state formaldehyde. It ultimately correlates with $(+)H_3N\text{-}O\text{-}CH_2(-)$, the proton tautomer of methoxyamine. The uppermost curve describes the best approach of NH_3 to the formaldehyde oxygen in the triplet state. Here the "in-plane" approach I is favored, with the two CH bonds bent out of the plane. The dashed line, somewhat higher in energy than the best approach in the triplet state, represents the corresponding cross-section of the hypersurface when the formaldehyde is kept planar.

At a surface crossing, the states share a common geometry. The energy of the lowest singlet state crosses that of the lowest triplet at $r_{(NO)} = 1.96$ Å when the singlet is constrained to the geometry of the best triplet approach. This crossing lies ap-