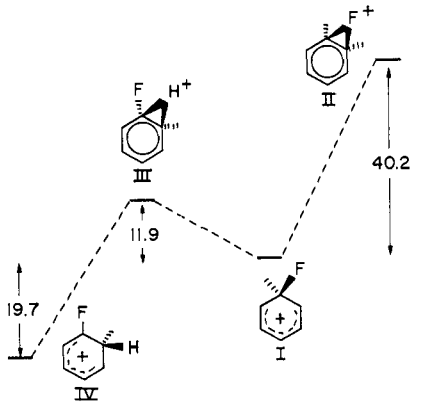

Figure 2. Stability of F^+ addition complexes (kcal/mol). 4-31G total energies: I, −329.36504; II, −329.30095; III, −329.34611; IV, −329.39641. Geometries for III and IV based on optimum STO-3G structures for bridged and open forms of protonated benzene.[4a] The fluorine in each case is attached with the same bond angles as the hydrogen replaced but with optimized (STO-3G) connecting bond lengths (1.346 and 1.324 Å, respectively).

energy maximum, some 40 kcal/mol above the open electrophilic adduct (I) (Figure 2). Although this latter ion rests in a potential well and is, in principle, a detectable intermediate, the calculations suggest 1,2-hydrogen migration—I → III → IV—to be a facile process, in line with experimental determination in related fluorine substituted benzenium ions.[20]

Finally we find fluorination at the ring face to be very unfavorable, in line with the high energy reported for the corresponding face protonated form of benzene.[4a]

Although the molecules dealt with here are too large to be considered at *ab initio* basis set levels beyond 4-31G, it is interesting to speculate on the possible consequences of such improvements. Hariharan, Lathan, and Pople[21] have noted that allowance for polarization-type functions on all centers contests the prediction of the 4-31G basis of a "classical" open equilibrium structure for the ethyl cation (with a barrier to proton migration of 7.3 kcal/mol) and suggests instead that the hydrogen bridged complex is the lower energy form (by 0.9 kcal/mol). The full brunt of the correction (8.2 kcal/mol) brings our value for the energy of proton migration in protonated benzene much closer to Olah's solution phase determination[2a] (12.4 kcal/mol *vs.* 10 ± 1 kcal/mol experimentally) and places further doubt on the stable existence of the open fluorine–benzene adduct (I), which now appears to be able to rearrange to the 2-fluorobenzenium ion (IV) with negligible barrier. It is more difficult to assess the effects of improved basis set description on the relative energies of the open and bridged fluorine benzene complexes (I and II, respectively). Comparison might be made with the recent study of Hariharan, Radom, Pople, and Schleyer on the $C_3H_7^+$ system.[22] Here the addition of polarization functions did little to alter the energy separation between symmetrically bridged (corner protonated cyclopropane) and open (1-propyl cation) structures.

(20) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 9241 (1972), and references therein.

(21) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972).

(22) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **96**, 599 (1974), and references therein.

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(23) Alfred P. Sloan Fellow, 1974–1976.

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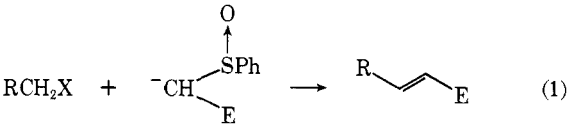
New Synthetic Reactions. Alkylative Elimination

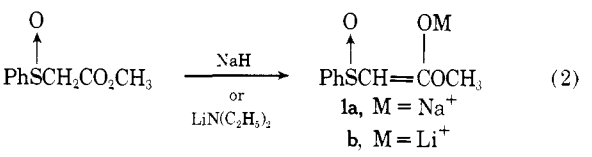
Sir:

The facile elimination of α-sulfinyl carbonyl compounds to their α,β-unsaturated derivatives (with complete absence of β,γ-isomers) suggested a new one-pot olefin synthesis of rather broad scope (see eq 1).[1,2]



(1)

While any sulfoxide anion in principle may be used, the high temperatures required for thermal eliminations of simple sulfoxides decrease their practicality. On the other hand, the facilitation of the elimination (as well as anion generation) by an α electronegative substituent makes this reaction an attractive approach. We wish to report the realization of this approach for the synthesis of α,β-unsaturated esters utilizing the anion of methyl 2-phenylsulfinylacetate[3–5] (see eq 2).



(2)

While anion formation proceeds well in many solvents (THF, DME, DMSO, or HMPA), alkylation with alkyl halides proceeds well only in dipolar aprotic solvents of which HMPA appears best. Carbon–carbon bond formation occurs at room temperature after which

(1) B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, **95**, 6840 (1973).

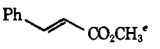
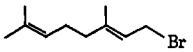
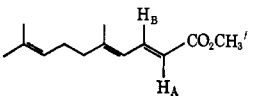
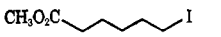
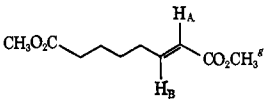
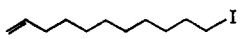
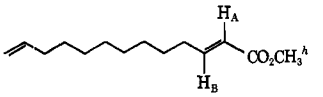
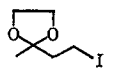
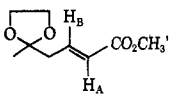
(2) For the first example of this net process see B. M. Trost and T. J. Fullerton, *J. Amer. Chem. Soc.*, **95**, 292 (1973). A two pot process utilizing selenium derivatives has appeared: K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, **95**, 6137 (1973). This method requires alkylation of the α-phenylselenyl ester and subsequent oxidation–elimination.

(3) Available by condensation of methyl bromoacetate with thiophenol [R. G. Hiskey and F. I. Carroll, *J. Amer. Chem. Soc.*, **83**, 4647 (1961)] followed by oxidation with sodium metaperiodate (methanol, room temperature, 18 hr) to give colorless solid, mp 46–48°; *Cf.* G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968).

(4) For alkylations of anions of β-ketosulfoxides see P. G. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966); O. P. Vig, K. L. Matta, J. M. Sehgal, and S. D. Sharma, *J. Indian Chem. Soc.*, **47**, 894 (1970).

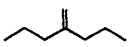
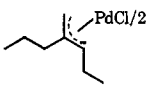
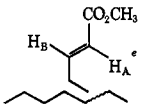
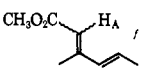
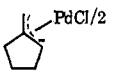
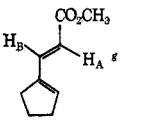
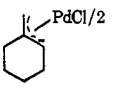
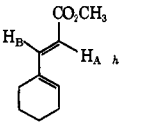
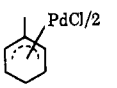
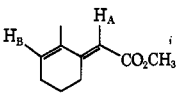
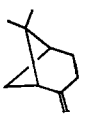
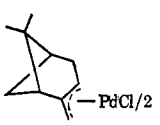
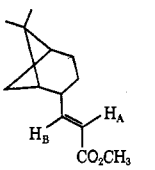
(5) In addition to aldol and Perkin and related condensations, other methods include Reformatsky reaction [M. Gaudemar, *Organometal. Chem. Rev. A*, **8**, 183 (1972); M. W. Rathke and D. F. Sullivan, *J. Amer. Chem. Soc.*, **95**, 3050 (1973)], phosphorus ylide [A. Maercker, *Org. React.*, **14**, 270 (1965)], phosphonate anion [J. Boutagy and R. Thomas, *Chem. Rev.*, **74**, 87 (1974)], and anions of α-silyl esters [K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **96**, 1620 (1974); S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, *Tetrahedron Lett.*, 1403 (1974)].

Table I. Alkyl Halides in Alkylative Elimination[a,b]

Entry	Halide	Reaction conditions (hr)	Product	Yield, %
1	$PhCH_2Br$	RT[i] (2) 75° (2)		30[c]
2		RT[i] (8) 90° (13)		86[c]
3		RT[i] (4) 85° (13)		82[c]
4		RT[i] (9) 90° (12)		80[d] (51[c])
5		RT[i] (6) 85° (12)		80[c]

[a] All new compounds have been fully characterized. [b] In these cases, the anion was generated by reaction of the sulfinyl ester with sodium hydride. [c] Yield represents pure compound isolated by chromatography or distillation. Yield has not been optimized. [d] Yield determined by nmr spectroscopy. [e] Confirmed by comparison to authentic sample. [f] δ_{HA} 5.78, δ_{HB} 7.52, J_{AB} = 15 Hz. [g] δ_{HA} 5.72, δ_{HB} 6.89, J_{AB} = 16 Hz. [h] δ_{HA} 5.70, δ_{HB} 6.86, J_{AB} = 16 Hz. [i] δ_{HA} 5.86, δ_{HB} 6.90, J_{AB} = 16 Hz. [j] RT, room temperature.

Table II. π-Allylpalladium Complexes in Alkylative Elimination[a]

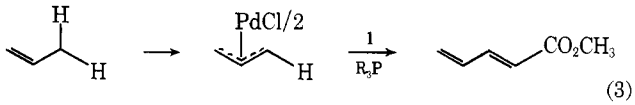
Entry	Olefin	Complex	Anion	Solvent	Phosphine	Time (hr), Temp	Product	% yield[b]
1			**1b**	DME	Ph_3P	12, RT[k] 2, 70°		57 (55)
2			**1b**	DME	Diphos[c]	22, RT[k] 1, reflux		41 (34)
3			**1b**	DME	Ph_3P	5, reflux		41 (27)
4			**1a**	DMSO	HMP[d]	12, RT[k] 6, 75°		71 (65)
5			**1a**	DMSO	HMP[d]	12, RT[k] 8, 75°		94 (81)
6			**1a**	DMSO	HMP[d]	12, RT[k] 6, 75°		89 (59)

[a] All new compounds have been fully characterized. [b] The yield of isolated pure product from the complex is listed. The numbers in parentheses represent the overall yield of product from olefin. [c] Diphos = $Ph_2PCH_2CH_2PPh_2$. [d] HMP = $[(CH_3)_2N]_3P$. [e] 7:3 *E*:*Z* of 4,5-double bond by vpc; *E*,*E* isomer, δ_{HA} 5.74, δ_{HB} 7.06, J_{AB} = 16 Hz; *E*,*Z* isomer, δ_{HA} 5.70, δ_{HB} 7.50, J_{AB} = 16 Hz. [f] *E*:*Z* 2:1 of 2,3-double bond by vpc; *E*,*E* isomer, δ_{HA} 6.05; *Z*,*E* isomer, δ_{HA} 5.56. [g] δ_{HA} 5.56, δ_{HB} 7.30, J_{AB} = 16 Hz. [h] δ_{HA} 5.76, δ_{HB} 7.28, J_{AB} = 16 Hz. [i] δ_{HA} 5.76 m, δ_{HB} 6.13. [j] δ_{HA} 5.76, δ_{HB} 7.28, J_{AB} = 16 Hz. [k] RT room temperature.

elimination proceeds by raising the temperature to 75–85° (see Table I). While optimization of conditions has not been attempted, improved yields are obtained when the elimination is allowed to proceed for 10–15 hr at approximately 80°. In the case of methyl 6-iodohexanoate, the yield of product jumped from 30% by employing a reaction time of 2 hr at 75° to 82% for a reaction time of 13 hr at 85°. Thus, it

anticipated that the yield for entry 1, Table I, can also be substantially improved. The sluggishness of the alkylation reaction requires reasonable reactive alkylating agents. Benzyl or allyl bromides and saturated alkyl iodides serve as suitable reagents.

Use of π-allylpalladium complexes, directly available from the corresponding olefin, offers a novel substitution at the allylic position of an olefin as repre-



(3)

sented by eq 3.[3,6] Table II summarizes the results. For these alkylative eliminations, a solution of the complex and phosphine (Pd/P = $^1/_2$) in THF, DME, or DMSO is allowed to stir at room temperature. A solution of **4** (M^+ = Na^+ or Li^+) in the same solvent is added and the stirring continued at room temperature. Subsequently, the temperature is raised to 70–75° to complete the reaction. Best results are obtained in DMSO with hexamethylphosphorustriamide as ligand (Table II, entries 4, 5, and 6).

Disubstituted olefins obtained from this reaction possess the *E* configuration (Table I, entries 1–5; Table II, entries 1, 3, 4, and 6) while trisubstituted double bonds are formed as a mixture of *E* and *Z* isomers (Table II, entry 2).[1] Nevertheless, the dienoate formed from 1-methylcyclohexene (Table II, entry 5) is apparently stereohomogeneous as determined by chromatographic and spectroscopic means. The *E* stereochemistry is assigned on the basis of europium shifts in the nmr spectrum in which the methyl portons are shifted only slightly (δ 1.84 → δ 2.32) upon addition of 41 mol % Eu(dpm)$_3$ while the allylic methylene protons are dramatically shifted (δ 3.02 → δ 5.75). The stereochemistry of the double bonds resulting from the π-allyl units reflects the stereochemistry of the precursor complex (Table II, entries 1 and 2).

The high stereoselectivity, regiospecificity, and chemospecificity associated with this approach offers some advantages over the alternative approaches.[5]

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health (NIGMS) for their generous support of our programs.

(6) B. M. Trost and T. J. Dietsche, *J. Amer. Chem. Soc.*, **95**, 8200 (1973); B. M. Trost, T. J. Dietsche, and T. J. Fullerton, *J. Org. Chem.*, **39**, 737 (1974); B. M. Trost and P. E. Strege, *Tetrahedron Lett.*, 2603 (1974).

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