after work-up, 180 mg of crude solid, mp 110–130°. This material, after recrystallization from *n*-hexane, gave 156 mg (78% yield) of white crystals, mp 141–143°, shown by glpc (4-ft SE-30, 250°) and ir, nmr, and uv spectra to be 9-phenylthiophenanthrene (10). No other reaction products could be detected.

9-Phenylthiophenanthrene (10) was prepared by reaction of the Grignard reagent of 9-bromophenanthrene[29] in benzene–ether with phenyl disulfide.[30] After repeated sublimations, chromatography over aluminium oxide, and recrystallization from methanol, a 40% yield of **10** was obtained, mp 134–136°. The material appeared to contain a trace of phenyl disulfide but ir, uv, and nmr spectra agreed with those of photolysis product **10**. Irradiation of **10** for 6.5 hr in ether solution in the presence of iodine led only to slow decomposition.

Anal. Calcd for $C_{20}H_{14}S$: C, 83.87; H, 4.93; S, 11.20. Found: C, 84.2; H, 4.8; S, 10.8.

Irradiation of phenyl sulfide (5h) (1.5 g in 550 ml of ether) in the Q-700 lamp for 3 hr in the presence of iodine led to formation of biphenyl (7.5% yield), dibenzothiophene (6h) (2.5% yield), and phenyl disulfide (5% yield) as determined by glpc (4-ft SE-30, 185°). These products were collected from the exit port of the gas chromatograph and either their uv or ir spectra shown to be identical with those of the authentic materials. When phenyl sulfide (500 mg in 115 ml ether) was irradiated for 5.3 hr in the absence of I_2 only biphenyl and phenyl disulfide could be identified.

Photolysis of 1,2-diphenylthioethene (5g) **and 1-(1-propenylthio)propene-1** (7) on a small scale in the presence of iodine failed to yield any cyclization products.

Dark reactions were not observed with the phenylthioethenes in ether solution. Addition of iodine likewise failed to promote a dark reaction. The reaction of **1b** at 80° in the dark in cyclohexane solution with AIBN initiator was examined; the material was consumed under these conditions but no benzo[*b*]thiophenes were formed. A photochemical reaction of **1b** carried out with an equimolar amount of phenyl disulfide gave a somewhat lower yield of **2b** and **3b** than a comparison reaction run without phenyl disulfide.

Registry No.—**1a**, 16336-45-1; **1b**, 16336-46-2; **2b**, 10371-50-3; **5a**, 1822-73-7; **5b**, 7594-43-6; **5c** (*cis*), 16336-50-8; **5c** (*trans*), 15436-04-1; **5d**, 16336-52-0; **5e**, 4922-47-8; **5f**, 6052-46-6; **5h**, 139-66-2; **8**, 16336-54-2; **10**, 16336-55-3.

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Chemistry of Enolates. V. Solvent Effects on the Activity of Carbanions[1]

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The kinetics and orientation in the alkylation of ketone enolates are extremely sensitive to solvent media. Alkylation rates and O/C product ratios are markedly increased by polyether solvents capable of chelating the accompanying metallic cation and by certain polar additives which exhibit first-order participation in the reaction kinetics. Increased electrical conductance of the enolate solutions parallels these chemical effects. In a specific solvent system, O/C product ratios are dependent on the steric requirements of both enolate and alkylating agent.

Much recent research has uncovered several factors affecting the reactivity and orientation of ambident[2] anions in nucleophilic reactions.[2-11] The factor producing the most significant effects is the reaction medium. Anions derived from phenols,[3-5] pyrroles,[8] ketones,[9] fluorene,[7] and malonic ester[6] exhibit similar behavior to changes in media. Two distinct effects are recognized: anion solvation by hydrogen bonding in protic solvents[3] and solvation of the accompanying cation by the bulk media,[7] the reaction product,[10] or an additive.[6]

Although ketone enolates are among the simpler ambident ions and are widely found in synthetic reactions, very little concerning their properties in solution or their orientation in the alkylation reaction has been reported. In this study ten dialkyl and alkyl aryl ketones are converted into the corresponding alkali metal enolates in a variety of solvent systems. Information on the nature of the enolates in solution is obtained from measurements of electrical conductivity, infrared and nmr spectra, boiling point elevation, orientation, and kinetics of alkylation.

Results and Discussion

Table I contains a summary of kinetic data for the alkylation of sodiodiphenylacetophenone in diglyme and mixed solvent systems. The alkylation of this ketone in these solvents occurs exclusively on oxygen to give enol ethers which, unlike ketonic products, do not compete in the solvation of the cation. Thus, excellent first-order dependence on enolate can be observed through the second and third half-lives of the reaction. A comparison of the alkylation of this ketone with that of butyrophenone in monoglyme is shown in Figure 1. Autocatalysis in the latter reaction causes the downward curvature of the line as the concentration of ketonic product increases.[10]

Most of the alkylations were carried out by a large excess of halide under pseudo-first-order conditions, although two runs made under second-order conditions gave linear plots (Figure 2) and rate constants in good agreement with those calculated from pseudo-first-order constants. These results are consistent with

(1) We gratefully acknowledge grants from the National Science Foundation in support of this work; the Department of Chemistry for an A-60 nmr spectrometer; an Eastman Kodak Co. Fellowship (T. J. R.); and an NSF Science Faculty Fellowship (E. F. F.).

(2) Anions which may undergo covalent bond formation at one or the other of two available positions: N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

(3) N. Kornblum, P. J. Berrigan, and W. J. LeNoble, *ibid.*, **85**, 1141 (1963); N. Kornblum, R. Seltzer, and P. Haberfield; *ibid.*, **85**, 1148 (1963).

(4) V. A. Zagorevsky, *J. Gen. Chem. USSR*, **27**, 3055 (1957); **28**, 488 (1958); *Chem. Abstr.*, **52**, 8108, 14572 (1958).

(5) D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, **80**, 1391 (1958); D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 6016 (1958).

(6) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *ibid.*, **82**, 2895 (1960). H. E. Zaugg, *ibid.*, **82**, 2903 (1960); **83**, 837 (1961).

(7) G. W. H. Scherf and R. K. Brown, *Can. J. Chem.*, **38**, 2450 (1960).

(8) C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **84**, 43 (1962).

(9) H. D. Zook and T. J. Russo, *ibid.*, **82**, 1258 (1960).

(10) H. D. Zook and W. L. Gumby, *ibid.*, **82**, 1386 (1960).

(11) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964).

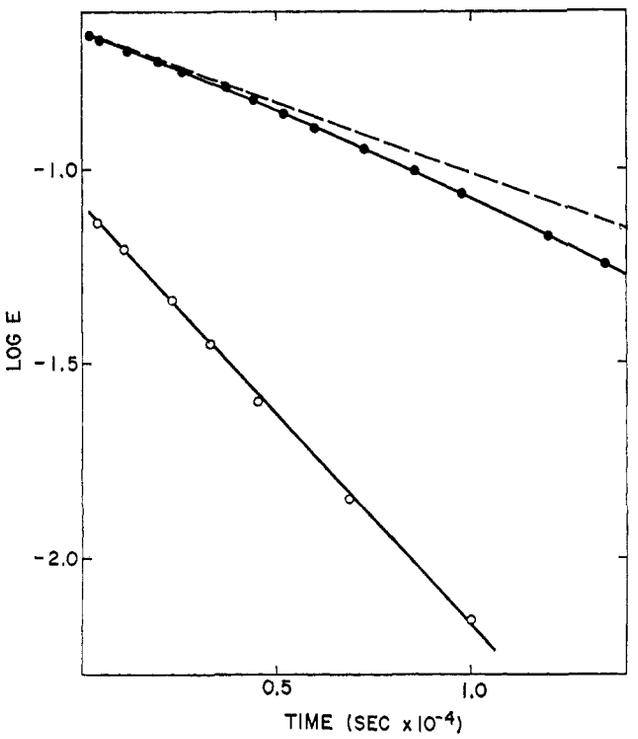


Figure 1.—Comparison of oxygen alkylation of an enolate with autocatalytic carbon alkylation: ○, ethylation of 0.073 *M* sodiodiphenylacetophenone in diglyme by 1.61 *M* ethyl bromide; ●, alkylation of 0.260 *M* sodiobutyrophenone in monoglyme by 1.39 *M* isobutyl bromide.

TABLE I

ALKYLATION OF SODIODIPHENYLACETOPHENONE IN DIGLYME AT 30°

Enolate, *M*	Halide (*M*)	Additive[a] (*M*)	$k_2 \times 10^4$, M^{-1} sec^{-1}
0.073	C_2H_5Br (1.72)		1.74
0.069	C_2H_5Br (0.19)		1.81
0.068	C_2H_5Br (0.28)	DMSO (0.14)	4.5
0.067	C_2H_5Br (0.26)	DMSO (0.27)	7.1
0.066	C_2H_5Br (0.35)	DMSO (0.43)	12.7
0.065	C_2H_5Br (0.27)	DMSO (0.65)	15.3
0.063	*n*-C_3H_7Br (1.41)		1.24
0.074	*n*-C_3H_7Br (0.21)		1.22
0.064	*n*-C_3H_7Br (0.66)	DMA (0.33)	3.4
0.061	*n*-C_3H_7Br (0.88)	DEA (0.16)	1.4
0.062	*n*-C_3H_7Br (0.66)	DEA (0.24)	2.0
0.064	*n*-C_3H_7Br (0.65)	DEA (0.33)	2.6
0.070	*n*-C_3H_7I (0.20)		9.4

[a] DMSO = dimethyl sulfoxide; DMA = N,N-dimethylacetamide; DEA = N,N-diethylacetamide.

those obtained in diethyl ether where the kinetic order for the halide at concentrations below 1 *M* was unity.[10]

Specific rates for alkylations of sodiobutyrophenone in several solvent systems are listed in Table II. The alkylation of butyrophenone is much faster than that of diphenylacetophenone; in diglyme at 30°, specific rates for ethylation by ethyl bromide are 91 × 10^{-4} and 1.7 × 10^{-4} M^{-1} sec^{-1}, respectively. Although the alkylations by low-molecular-weight bromides and iodides were too rapid at 30° for precise measurement, a comparison of solvents was made by alkylations with chlorides and branched-chain bromides. The expected order of reactivity for the halides was observed. Solvents are listed in order of increasing effectiveness. Comparisons with four halides show

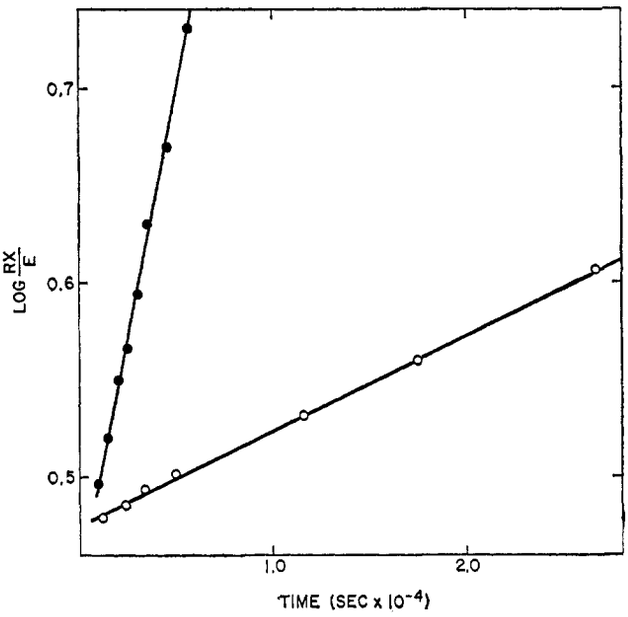
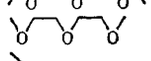
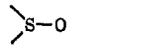


Figure 2.—Propylation of 0.074 *M* sodiodiphenylacetophenone in diglyme at 30°: ○, with 0.214 *M* *n*-propyl bromide; ●, with 0.197 *M* *n*-propyl iodide.

TABLE II

MEDIUM EFFECTS IN THE ALKYLATION OF SODIOBUTYROPHENONE

Solvent	$k_2 \times 10^4$, M^{-1} sec^{-1} [a]				
	C_2H_5Br	*n*-C_4H_9Br	*i*-C_4H_9Br	*i*-$C_5H_{11}Br$	*n*-C_3H_7Cl
	0.01		0.00043		
				0.05[b]	
			1.1[c]	2.9[d]	0.02[e]
		6.3		2.8	
	91	38	4.9	8.1	0.07
					76.1[f]

[a] Obtained under pseudo-first-order conditions from 0.14–0.18 *M* enolate and excess halide. [b] 0.34 in the presence of 0.43 *M* hexamethylphosphoramide. [c] 2.6 in the presence of 0.82 *M* N,N-dimethylacetamide. [d] No change in the presence of 0.54 *M* dimethylcyanamide. [e] 0.15 in the presence of 0.61 *M* dimethyl sulfoxide. [f] Unpublished results of Dr. J. A. Miller of this laboratory.

that diglyme is three to five times as effective as monoglyme and 10^4 times as effective as ethyl ether. Dimethyl sulfoxide exhibits a rate enhancement of 10^3 over diglyme. The observed order among the ethers suggests chelation of the cation. Diglyme can form two five-membered chelate rings, the optimum size for stability.[12] Two diglyme molecules could form six-coordinate sodium ion which has been observed in complexes with salicylaldehyde.[13] The terminal ethyl groups in diethylene glycol diethyl ether hinder chelation. Probably the best evidence is found in a comparison of 1,2-dimethoxyethane and 1,3-dimethoxypropane; separation of the ether functions by an additional carbon atom produces a 60-fold decrease in the rate of isoamylation.

This explanation of the role of the solvent ignores differences in dielectric properties of the media. Among

(12) J. L. Down, J. Lewis, B. Moore, and G. Wilkinson, *J. Chem. Soc.*, 3767 (1959).

(13) N. V. Sidgwick and F. M. Brewer, *ibid.*, 2379 (1925).

TABLE III
MOLAR CONDUCTANCES OF ENOLATES

Sodium enolate	M	Solvent system (M)[a]	Λ_m, cm² mol⁻¹ ohm⁻¹
Acetophenone	0.10	Diethyl ether	0.000[b]
Diphenylacetophenone	0.016	1,2-Dimethoxyethane	0.12
Butyrophenone	0.18	1,3-Dimethoxypropane	0.002
	0.10	1,2-Dimethoxyethane	0.035
	0.10	N,N-Dimethylacetamide (0.98)	0.082
	0.10	N-Methylpyrrolidone (0.95)	0.085
	0.10	N,N-Dimethylcyanamide (0.98)	0.244
	0.10	Dimethyl sulfoxide (1.28)	0.250
	0.10	Hexamethylphosphoramide (0.94)	0.255

[a] Molar concentration of additive in dimethoxyethane. [b] Reference 14, $R > 2.5 \times 10^6$ ohms.

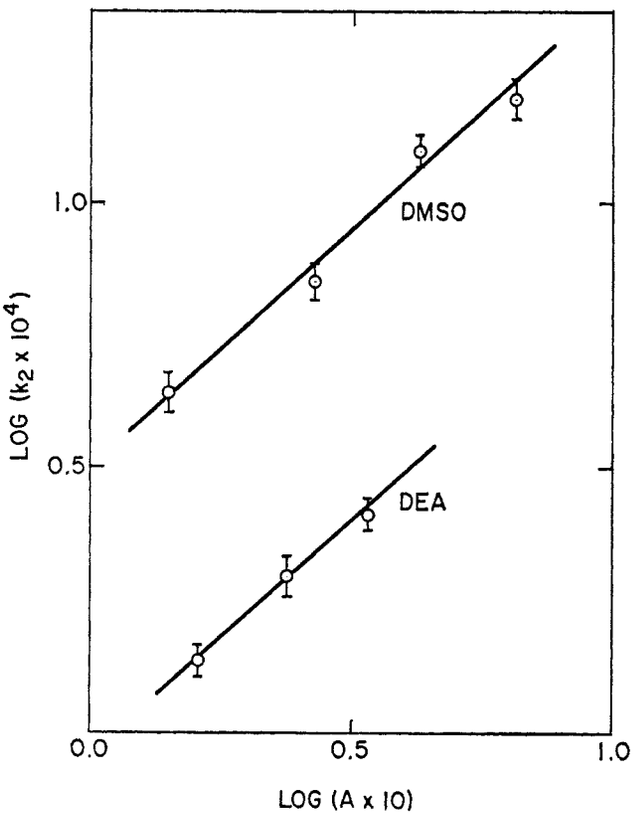


Figure 3.—Kinetic order in additive: ethylation of sodiodiphenylacetophenone in diglyme–dimethyl sulfoxide and propylation of this enolate in diglyme–diethylacetamide.

the ethers listed, the variation in dielectric constant is small; *e.g.*, the value for diglyme is only 0.07 larger than that for diethylene glycol diethyl ether. In the alkylation of sodio-*n*-butylmalonate, monoglyme as an additive was six times more effective than tetrahydrofuran even though the two ethers have nearly identical dielectric constants.[6,12] The small differences cannot account for the large variation in the ability to promote alkylation.

Pronounced rate enhancement was observed when alkylations of diphenylacetophenone (Table I) and butyrophenone (Table II, footnotes *b–e*) were conducted in the presence of dimethyl sulfoxide, hexamethylphosphoramide, and N,N-dialkylacetamides. These additives characterized by the presence of a highly polar bond to an oxygen atom had proved effective catalysts in alkylations of benzene solutions of sodio-*n*-butylmalonate.[6] Their effectiveness in relatively small concentrations suggests a specific solvation of the cation. Consistent with this view is the finding that the rate of alkylation of sodiodiphenylacetophenone exhibits first-order dependence on the additives, N,N-diethylacetamide and dimethyl sulfoxide. The participation order, n, is defined by the relation $k_2 = k_2'[A]^n$ where k_2 is the second-order specific rate (Table I) and k_2' is the additive-independent specific rate. Plots of log k_2 *vs.* log A for ethylations in the presence of dimethyl sulfoxide and propylations in the presence of diethylacetamide were linear (Figure 3) with approximately unit slopes.

Conductance Studies.—Sodium enolates of ketones are nonconductors in diethyl ether although sodium triphenylmethide has molar conductances of 0.05–0.72 in this solvent.[14] Data summarized in Table III show that the conductance increases with the solvating ability of the polyether and the polar additives. In Figure 4 is plotted the logarithm of molar conductance *vs.* the logarithm of enolate concentration for a solution of sodiobutyrophenone in monoglyme. The slope of the line is −0.5, a value indicative of the dissociation of a species A^+B^- into ions. In view of the ebulliometric study of sodiobutyrophenone, which shows that the enolate is a trimer, a possible structure for B^- is a triple ion, $Na^+[Na_2(enolate)_3]^-$.

Conductances for the solutions containing the five polar additives are included in Figure 4. This comparison shows the two structurally similar carboxamides, N-methylpyrrolidone and N,N-dimethylacetamide, to have an approximately equal ability to increase the conductivity although they are not so effective as hexamethylphosphoramide, dimethyl sulfoxide, and dimethylcyanamide. With the exception of the last compound, the order of the effectiveness of these additives parallels the order in catalyzing the alkylation of the enolates. Triethylenediamine and N,N,N,N-tetramethylethylenediamine did not increase the conductance. Catalytic action by these amines was not investigated because of their posssible alkylation. However, Zaugg[6] has shown that pyridine is less effective than monoglyme in catalyzing the alkylation of sodio-*n*-butylmalonate, and Garst[11] reported that *n*-propylamine is less effective than either monoglyme or diglyme in lowering the π–π^* transition of sodium benzophenone ketyl.

Boiling point elevations for 0.5 *m* solutions of sodiobutyrophenone in 1,2-dimethoxyethane correspond to average aggregation numbers of 2.5–2.7, values 16%

(14) D. G. Hill, J. Burkus, S. M. Luck, and C. R. Hauser, *J. Amer. Chem. Soc.*, **81**, 2787 (1959).

TABLE IV
ORIENTATION IN THE ALKYLATION OF ENOLATES

$C_6H_5C(O^-M^+)=CRR'$

R	R′	M^+	Solvent	O/C alkylation ratio[a] MeI	Allyl Br	EtX[b]	*n*-PrX[b]	*i*-AmBr	EtTos
H	C_6H_5	Na	DME		0.0	0.0		0.0	
CH_3	CH_3	Na	Et_2O	0.0			0.0		0.63[c]
		Na	DME			0.19	0.25	0.36	
		Na	Diglyme	0.0	0.05	0.16	0.27		1.2[d]
C_2H_5	CH_3	Na	Diglyme		0.2	0.61			2.4
C_2H_5	C_6H_5	Na	Diglyme			0.76			3.0
C_6H_5	C_6H_5	K	*t*-BuOH	0.04		1.4	2.5[e]		
		Na	*t*-BuOH			1.8[g]			
		Na	Diglyme	0.09[f]		18	>100		
C_6H_5	Mesityl	K	*t*-BuOH			>100	>100		

[a] Exclusive of small quantities of dehydrohalogenation product. [b] Alkyl bromides were used except in *t*-butyl alcohol where the alkylating agent was the iodide. [c] Ethyl sulfate gave 0.34. [d] Also for ethyl sulfate and MeTos. [e] Ref 12. [f] O/C = 1.0 in 50:50 diglyme–DMSO. [g] In one series of experiments, the O/C ratio was dependent on the concentration of enolate; *M* of ketone, *M* of *t*-OBu, % alkylation, and O/C ratio for five solutions are as follows: 0.24, 0.25, 70, 1.8; 0.21, 0.24, 71. 1.8; 0.059, 0.110, 54, 1.3; 0.030, 0.104, 56, 1.2; 0.011, 0.037, 21, 0.01.

below those measured in diethyl ether.[10] These results, together with the increased electrical conductivities suggest that the effective cation-solvating media break up enolate–cation aggregates into smaller ions.

O/C Orientation.—The usual synthetic processes for the alkylation of acetophenone, deoxybenzoin, and their homologs lead to high yields of C-alkyl products. However, the procedures are not designed to detect enol ethers which are easily lost by hydrolysis. Several instances of O alkylation of ketones have been reported.[15-17] To determine structural and solvent effects on orientation, analyses by ir and vpc techniques of t_∞ samples from several of the kinetic runs were made, and other alkylations were conducted solely for this purpose. The results are listed in Table IV.

The O/C alkylation ratio is quite sensitive to changes in the structure of the enolate, the structure of the alkylating agent and the solvent. Isobutyrophenone and deoxybenzoin resemble the simpler *n*-alkyl phenyl ketones in that alkylation by halides in diethyl ether leads exclusively to C-alkyl products. In polyether solvents isobutyrophenone gives as much as 27% enol ether depending on the structure of the halide, while only C alkylation is observed for deoxybenzoin even with isopropyl iodide (see Experimental Section). As the size of the substituent groups at the α position in the enolate increases, the proportion of O alkylation becomes significantly larger until, in the propylation of diphenylacetophenone, the enol ether is the sole product.

Carbon alkylation results in an sp^3-hydridized carbon atom with the three substituents at 109° whereas oxygen alkylation results in an sp^2-hybridized carbon with only two groups forming a much larger angle. Thus, the effects of the geometry of the products on the transition state favor O alkylation as the substituents on the enolate and halide increase in size. The halides are listed from left to right in Table IV in order of increasing steric requirement, and the ketones from top to bottom in increasing hindrance to C alkylation. Steric factors in both reagents are important; O/C ratios increase from left to right and from top to bottom. The high ratios observed with ethyl sulfate and methyl and ethyl tosylates are in accord with the known ability of these reagents to alkylate the atom of higher electronegativity in an ambident ion.[18] This preference of a highly electrophilic reagent has been attributed to a gain in electrostatic stability in the transition state.[2,19]

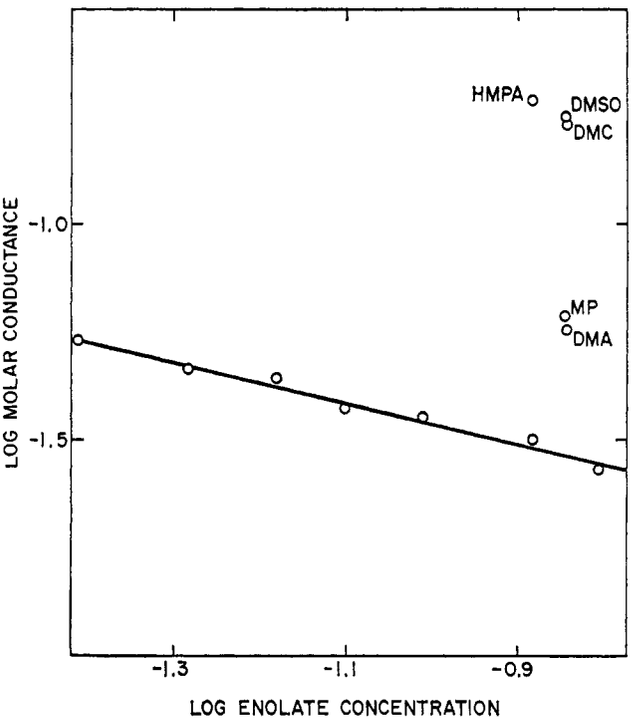


Figure 4.—Conductance of sodiobutyrophenone in monoglyme. Effect of concentration and additives (*cf.* Table III).

The large decrease in O/C ratio for the ethylation of diphenylacetophenone as the solvent is changed from diglyme to *t*-butyl alcohol was reported in an earlier communication[9] and now has been confirmed for methylations and propylations of this ketone. Although Rinderknecht[15] isolated the C-propyl product, α,α-diphenylvalerophenone, in about 6% yield when the alkylation was conducted in *t*-butyl alcohol, com-

(15) H. Rinderknecht, *J. Amer. Chem. Soc.*, **73**, 5770 (1951).
(16) N. Sperber, R. Fricano, and D. Papa, *ibid.*, **72**, 3068 (1950).
(17) G. Wash, B. Shive, and H. L. Lochte, *ibid.*, **63**, 2975 (1941).
(18) K. Auwers, *Chem. Ber.*, **45**, 994 (1912), *Ann. Chem.*, **393**, 338 (1912); H. Stetter and W. Dierichs, *Chem. Ber.*, **85**, 61 (1952).
(19) M. Bersohn, *J. Amer. Chem. Soc.*, **83**, 2136 (1961).

plete O propylation to 1-propoxy-1,2,2-triphenylethylene resulted in diglyme both in the presence and absence of N,N-dialkylacetamides. Kornblum has presented convincing evidence that similar orientation in phenoxide ions is the result of hydrogen bonding of the anion in protic solvents.[3]

More effective hydrogen bonding resulting in increased hindrance and lower nucleophilicity at the oxygen atom would be expected at lower enolate concentrations. In one series of experiments in *t*-butyl alcohol the O/C ratio decreased markedly as the concentration of enolate was decreased from 0.24 to 0.011 *M* (Table IV, footnote *g*). In contrast, dilution in aprotic solvents ordinarily favors alkylation at the more electronegative atom.[8,20]

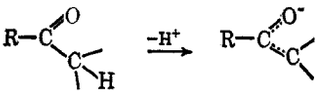
In aprotic solvents, the O/C ratio depends primarily on the ability of the solvent to solvate the cation. In ethyl ether where the enolate consists of trimeric species, nucleophilicity at oxygen is low and carbon alkylation occurs probably by a six-centered transition state.[10,21] A solvate of sodiodeoxybenzoin isolated from monoglyme has been shown by nmr and equivalent weight determinations to contain one molecule of solvent per ion pair;[22] yet even in this solvent the aggregation number is 2.7, and appreciable C alkylation occurs. In the presence of molecules which can better solvate the cation and in this way free the anion, alkylation at the more nucleophilic oxygen is preferred. Thus, the medium effect on the activity of the anion operates indirectly *via* the cation.

The solubilities of sodiodiphenylacetophenone in ether, monoglyme, and diglyme are 0.004, 0.016, and >0.092 *M*, respectively. These solubilities parallel the ability of the solvent to enhance electrical conductivity and alkylation rate. A similar correlation between solubility and N alkylation of pyrrylpotassium has been observed.[8]

It is believed that the observed aprotic medium effects originate through variations in the enolate–cation interaction. Thus, the better chelating polyethers, the polar amides, the very polar dimethyl sulfoxide, and hexamethylphosphoramide all interact with the sodium ion, thereby decreasing the degree of its interaction with the enolate. Alkylation reactions are faster because the dissociated enolate, unencumbered by the cation, can better function as a nucleophile. Oxygen alkylation increases at the expense of carbon alkylation because in the dissociated enolate the charge density is greatest at the oxygen atom. Finally, the solvated cation and dissociated enolate are electrical conductors.

Infrared and nuclear magnetic resonance spectra of enolate solutions can be interpreted to show that the excess negative charge is localized on the oxygen atom of the anion as expected on the basis of electronegativity. The large shift in the carbonyl absorption toward lower frequencies and an nmr shift indicative of diamagnetic anisotropic deshielding for the remaining hydrogens of an enolized methyl ketone are explainable on this basis.

The formation of an enolate can be followed by the disappearance of the carbonyl peak at 1725–1667 cm^{-1} and the appearance of a peak at 1610–1560 cm^{-1} corresponding to the change shown.



It is interesting to note that the enolate resembles a carboxylate anion. The ionization of a carboxylic acid similarly results in the disappearance of the carbonyl frequency and the emergence of a band between 1610 and 1560 cm^{-1} attributed to the antisymmetrical vibrations of the $-COO^-$ structure.[23] By analogy, this characteristic band of enolate solutions may be attributed to asymmetrical stretching of the structure containing the delocalized negative charge. Although the force constant for a bond is a function of both bond order and polarizability, numerous linear correlations have been made in terms of bond order alone.[24] By an extension of these correlations, the bond order for pinacolone decreases from 0.90 ($\nu_{C=O}$ 1710 cm^{-1}) to 0.73 ($\nu_{C=O}$ 1575 cm^{-1}) as a result of enolate formation. This result implies a much reduced π-bond density between carbon and oxygen. The frequency shift is in the same direction but greater in magnitude than those found when other typical electron releasing groups are conjugated with the carbonyl.[25] Another spectral feature similar to that observed for benzoic acid is the disappearance of the out-of-plane bending vibrations of ring hydrogens at 687 and 755 cm^{-1} when acetophenone is converted into its enolate.

The nmr spectra of pinacolone and its sodium enolate exhibit significant differences. The *t*-butyl hydrogens at 1.13 ppm are shifted upfield to 1.07 ppm as expected by increased electron density at oxygen. The 2.11-ppm peak corresponding to the methyl hydrogens is not present in the enolate but is replaced by a peak at 3.10 ppm representing the two remaining hydrogens. Estimates of relative magnitudes of the peaks are in accord with this assignment. The large downfield shift can be explained if it is assumed that the carbon atom to which these protons are attached cannot rotate freely. Although negative charge on oxygen should shield the hydrogen atoms, the effect is overcome by the diamagnetic anisotropic deshielding made possible by the rigid structure.

Sodium enolates of butyrophenone and diphenylacetophenone are cleaved by oxygen to give sodium benzoate and carbonyl compounds. Diphenylacetophenone gives a quantitative yield of sodium benzoate and benzophenone. Heretofore, only the former product of such cleavages has been isolated,[26] for most enolates give enolizable aldehydes and ketones which are further degraded. For example, sodiobutyrophenone gives propionaldehyde which undergoes a proton transfer with the original enolate to produce butyrophenone (23%) and propionaldehyde enolate.

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Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

Solvents.—1,3-Dimethoxypropane was prepared in 81% yield from 221 g of 51% sodium hydride dispersion in mineral oil, 152 g of Eastman trimethylene glycol, and 613 g of methyl iodide. The hydride was stirred with 500 ml of tetrahydrofuran during the dropwise addition of a solution of the glycol in 200 ml of the same solvent. The condenser was then cooled to Dry Ice temperatures for the addition of the methyl iodide. Finally the mixture was refluxed overnight, sodium iodide filtered, and washed with five 100-ml portions of tetrahydrofuran, and the product fractionally distilled from a small piece of sodium. The 1,3-dimethoxypropane, bp 103.2° (730 mm), was separated from a small amount of lower boiling impurity by refractionation through a spinning-band column.

Eastman diethylene glycol diethyl ether was first chromatographed on a 54 × 1.5 cm column of alumina to remove peroxides and effect preliminary drying. Fractional distillation from lithium aluminum hydride gave ether, bp 65–66.0° (6.3 mm).

Diethyl ether, monoglyme [bp 83.7° (745 mm)] and diglyme [bp 55.0° (10 mm)] were fractionally distilled from lithium aluminum hydride. Preliminary drying of the glyme solvents (Ansul Chemical Co.) was accomplished by stirring and heating overnight with calcium hydride.

The following solvents were distilled from calcium hydride prior to their use: hexamethylphosphoramide (Aldrich), bp 104.9° (9.5 mm); N,N,N,N-tetramethylethylenediamine (Rohm and Haas), bp 119° (735 mm); N-methyl-2-pyrrolidone (Antara), bp 81.5° (11 mm); dimethyl sulfoxide (Crown Zellerbach), bp 71.5° (10 mm); and N,N-dimethylcyanamide (American Cyanamid), bp 118° (217 mm). The following solvents were fractionated and stored over anhydrous magnesium sulfate: N,N-dimethylacetamide (Eastman), bp 165° (725 mm); and N,N-diethylacetamide (Eastman), bp 66° (10 mm).

Ketones.—Eastman butyrophenone was stirred for several days with activated charcoal and anhydrous magnesium sulfate. Fractional distillation gave yellow material, bp 55° (1.5 mm). The yellow color and a trace of higher boiling material (glpc analysis) were completely removed by chromatography on a column of alumina. α-Methylbutyrophenone, bp 98° (18 mm), was made from propiophenone, sodium hydride, and ethyl bromide in diglyme.

α,α-Diphenylacetophenone was prepared by adding in small portions a solution of 50 g of desyl chloride[27] in 150 ml of dry benzene to a suspension of 32 g of aluminum chloride in 100 ml of benzene. The mixture was refluxed for 1 hr and poured onto ice. A benzene extract of the product was evaporated to give 60 g of crude solid. Two crystallizations from ethanol gave white needles, mp 135–137° (lit.[28] mp 136°).

α,α-Dimethylbutyrophenone and 1-ethoxy-1-phenyl-2-methylpropene were prepared by stirring for 2 days 28 g of ethyl *p*-toluenesulfonate and 200 ml of 0.35 *M* sodioisobutyrophenone. The enolate was made over a period of 36 hr at 85° by stirring a twofold excess of sodium hydride with a diglyme solution of the ketone. An infrared spectrum of the enolate solution showed no carbonyl absorption. Fractional distillation of the alkylation mixture through a spinning-band column gave one fraction, 1.54 g, of enol ether, bp 57° (2 mm), with characteristic vinyl ether absorption at 1126 and 1042 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.88; H, 9.15.

The last fraction, 3.56 g, was dimethylbutyrophenone, bp 79–80° (2 mm), with strong absorption at 1661, 1163, and 954 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.78; H, 9.16.

α-Ethyldeoxybenzoin was prepared in 80% yield by refluxing for 24 hr 750 ml of 0.084 *M* sodiodeoxybenzoin in monoglyme and 10 ml of ethyl iodide. The enolate was obtained by stirring for 5 hr 4.0 g of sodium hydride and 16.5 g of deoxybenzoin in 900 ml of dry monoglyme. After alkylation, solvent was removed through a short column, and the precipitated sodium iodide was extracted with ether. Removal of ether and recrystallization of the solid from ethanol gave 11.2 g of white crystals, mp 53.5–55.0° (lit.[29] mp 58°). α-Mesityldeoxybenzoin, mp 113–115°, was prepared as described previously.[30]

Alkylation of Enolate Solutions.—The apparatus for the preparation, storage, and alkylation of enolates was essentially that used in an earlier study.[31] Sodium enolates in polyether solvents were made from the ketones and sodium hydride as described for solutions in diethyl ether.[10] Enolate formation from α,α-diphenylacetophenone was complete within a few minutes as evidenced by vigorous evolution of hydrogen, immediate formation of a yellow color, and the disappearance of carbonyl absorption in the infrared. With butyrophenone, hydrogen evolution was slow, and stirring was continued for 7 days. Concentrations determined by quenching aliquots in water and titrating with standard acid were in excellent agreement with those calculated from the amounts of ketone and solvent used. Because phenolphthalein gave premature end points in aqueous diglyme and diethylene glycol diethyl ether, bromophenol blue was used in experiments with these solvents. The kinetic reaction vessel was thoroughly flamed in a stream of nitrogen before each run. Unless otherwise indicated, kinetic measurements were made at 30.00 ± 0.05°. Samples at t_∞ in ether or monoglyme were taken directly without hydrolysis for product studies by glpc.

Product Studies.—A typical procedure for ethylation in *t*-butyl alcohol consisted of dissolving 0.0125 g-atom of sodium or potassium in 50 ml of dry alcohol, adding an equivalent amount of ketone followed by an excess of alkyl halide, and refluxing overnight. Solvent was removed under vacuum after the addition of a few milliliters of water. The residue was triturated with water, washed free of halide ion, dried in a desiccator, weighed, and dissolved in carbon tetrachloride for infrared analysis. 1,2,2-Triphenyl-1-butanone, 1,2,2-triphenyl-1-ethoxyethene, and 1,2,2-triphenyl-1-propoxyethene, the C-ethyl, O-ethyl, and O-propyl alkylation products of α,α-diphenylacetophenone, were prepared as described[15] and used as references for quantitative infrared analyses. Beer's law plots for α,α-diphenylacetophenone and its O- and C-ethyl derivatives were constructed at 1224, 1208, and 1092 cm^{-1}. The results of the ethylations are listed in Table IV. A product study of the propylation of this ketone in diglyme was carried out on the t_∞ sample from a kinetic run. Excess *n*-propyl bromide was removed under vacuum at 50°. To the residue was added 300 ml of water to precipitate the reaction product which was then filtered, washed with water, and dried in a desiccator. The infrared spectrum was identical with that of pure 1-propoxy-1,2,2-triphenylethene except for an extremely small carbonyl-stretching peak. In a similar manner, product studies were carried out for the propylation with a twofold excess of *n*-propyl bromide, with *n*-propyl iodide, with added N,N-dimethylacetamide, and with added N,N-diethylacetamide. In all cases, only O alkylation resulted. Methylation by methyl iodide of the potassium enolate formed from 5.0 g of this ketone and 1.1 g of potassium in 75 ml of dry *t*-butyl alcohol gave a product whose spectrum was consistent with C methylation except for a very small peak at 1089 cm^{-1}. This peak disappeared when the product was refluxed with ethanolic hydrogen chloride.

Isopropylation of deoxybenzoin was carried out by refluxing overnight a solution of 0.023 g-atom of potassium, 0.015 mol of ketone, and 20 ml of isopropyl iodide in 100 ml of dry *t*-butyl alcohol. The solvent was removed under vacuum to give only the C-alkyl ketone (95%). The infrared spectrum gave a single carbonyl peak and no absorbance characteristic of enol ether. The spectrum was unchanged when a sample was refluxed for 2 hr with dilute hydrochloric acid. One recrystallization from ethanol gave α-isopropyldeoxybenzoin, mp 71–73° (lit.[32] mp 71–72°).

Glpc analyses were made at 80–160° with a spiral glass column packed with methylsilicone (GE SF-96) on 100–140 mesh Gaschrom Z. Under these conditions the enol ethers did not undergo decomposition or rearrangement. Enol ether peaks were identified by hydrolysis of a second sample with 1 drop of concentrated hydrochloric acid prior to chromatographic analysis. The enol ether peak vanished in the second chromatogram, and the small peak representing original ketone increased proportionately.

(27) A. M. Ward, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 159.

(28) R. Anschutz and P. Forster, *Ann. Chem.*, **368**, 92 (1909).

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(32) M. Tiffeneau and A. Orekhoff, *Bull. Soc. Chim. Fr.*, [4] **33**, 211 (1923).

The O/C product ratios were calculated directly from peak areas. Thermal response values relative to acetophenone were determined for a number of the products, but their use was not warranted.

Conductivity Measurements.—Resistances were measured in a 25-ml conductivity cell surmounted on the kinetic apparatus in place of the automatic sampling buret. Solvents and solutions were forced into the cell by increasing the nitrogen pressure in the reaction vessel. The cell was drained under a nitrogen atmosphere and flushed thoroughly with dry solvent before and after measurements were made. Resistances were measured with a Wheatstone bridge, 5000-cps audiofrequency oscillator, and earphones to detect the null point.

Cleavage of Sodiodiphenylacetophenone by Oxygen.—Immediate formation of solid, evolution of heat, and fading of yellow color occurred when oxygen gas was bubbled through a solution of 11.1 mmol of enolate in 150 ml of diglyme. After 12 hr of oxygen treatment, the semisolid mixture was dissolved in 100 ml of water to give a clear solution which required only 0.4 mmol of standard acid for titration to phenolphthalein. The solution was steam distilled to give 1.84 g (92%) of benzophenone, mp 43–46°. The infrared spectrum was superimposable on that of an authentic sample of benzophenone. The steam distilland was made alkaline with potassium carbonate solution and extracted with three 100-ml portions of ether. Evaporation of these extracts yielded no more than a trace of oily substance. The alkaline layer was acidified with concentrated hydrochloric acid and extracted with three 100-ml portions of ether. Evaporation of these extracts left 1.32 g (99%) of white solid, mp 120–122.5°. This substance did not depress the melting point of pure benzoic acid.

Registry No.—Sodiodiphenylacetophenone, 16282-12-5; sodiobutyrophenone, 16310-84-2; α-methylbutyrophenone, 938-87-4; α,α-diphenylacetophenone, 1733-63-7; α,α-dimethylbutyrophenone, 829-10-7; 1-ethoxy-1-phenyl-2-methylpropene, 16282-15-8; α-ethyldeoxybenzoin, 16282-16-9; α-mesityldeoxybenzoin, 16282-17-0.

Condensations at Methyl Groups of Phenyl *o*- and *p*-Tolyl Sulfones with Electrophilic Compounds by Sodium Amide. Truce–Smiles Rearrangement[1]

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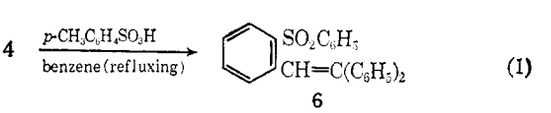
Ionizations of methyl hydrogens of phenyl *o*- and *p*-tolyl sulfones were effected by sodium amide in liquid ammonia to form sodio salts, which were condensed with benzyl chloride, 1,4-dibromobutane, benzophenone, and methyl benzoate to give corresponding derivatives. Ionization of the phenyl *o*-tolyl sulfone occurred more slowly than that of the *para* isomer. The addition reactions of the sodio salts with benzophenone were kinetically controlled. The condensations of the sodio *o*-tolyl sulfone with the electrophilic compounds represent trapping of the intermediate carbanion in the Truce–Smiles rearrangement of the sulfone to form a sulfinic acid, which was observed in low yield through the sodio salt in liquid ammonia and in good yield in refluxing tetrahydrofuran. The benzyl derivative of the *o*-tolyl sulfone underwent this type of rearrangement with *n*-butyllithium. Di-*p*-tolyl sulfone was benzylated at one of its methyl groups by means of sodium amide. The method appears to be quite general.

Although base-catalyzed condensations at the α carbon of dimethyl sulfone and other sulfones with electrophilic compounds are well known,[2] related reactions at the methyl groups of *o*- and *p*-tolyl sulfones have rarely been reported. The present investigation was concerned with such a study of phenyl *o*- and *p*-tolyl sulfones; the former sulfone promised to be of particular interest because it can undergo the base induced Truce–Smiles type of rearrangement.

Results with Phenyl *o*-Tolyl Sulfone.—This compound (**1**) was converted by sodium amide in liquid ammonia into sodio salt **1′**, which was condensed with benzyl chloride, 1,4-dibromobutane (0.5 mol equiv), benzophenone, and methyl benzoate to form **2**, **3**, **4**, and **5**, respectively (Scheme I).

The yields of the benzyl derivative **2**, the bis derivative **3**, and the addition product **4** were dependent on the conditions employed (see Discussion); the best yields obtained were 61, 58, and 76%, respectively. The yield of the benzoyl derivative **5** was dependent on the proportions of the reactants since, similar to other Claisen-type acylations and aroylations,[3] the product **5** was converted in the reaction mixture into its sodio salt; this last step was effected by either sodio sulfone **1′** or sodium amide. When 2 mol equiv of sodio sulfone **1′**/1 mol equiv of methyl benzoate was used (last step effected by **1′**), the yield of **5** based on the ester was 50%;[4] when 1 extra equiv of sodium amide was used to effect the last step, the yield of **5** based on sulfone **1** was 34%.

The structures of the condensation products were supported by analyses and absorption spectra. The structure of adduct **4** was confirmed by dehydration to form unsaturated sulfone **6** in 86% yield (eq 1).



6 (1)

The infrared spectra of the products were similar to those of the starting sulfone **1** with certain significant differences (Table I).[5] The spectrum of carbinol sulfone **4** showed a strong hydroxyl peak, which was absent in that of the dehydration product **6**. The spectrum of the keto sulfone **5** exhibited a strong carbonyl peak.

(1) Supported by U. S. Public Health Service Research Grant No. CA 04455 from the National Cancer Institute and by the Army Research Office (Durham).

(2) See especially L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961), and D. F. Tavares and P. F. Vogt, *Can. J. Chem.*, **45**, 1519 (1967), and references cited therein.

(3) For related aroylations of ketones with esters by sodium amide, see *Org. Reactions*, **8**, Chapter 3 (1954).

(4) Theoretically one-half of sulfone **1** would be regenerated; actually the yield of **5** based on starting sulfone **1** used minus that recovered was 38%.

(5) See R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966.