Registry No.—**1**, 27729-87-9; **2**, 27729-88-0; **3**, 27729-89-1; **4**, 27729-90-4; **5**, 27729-91-5; **6**, 27729-92-6; **7**, 27729-93-7; **8**, 27729-94-8; **9**, 27729-95-9; **10**, 27729-96-0; **11**, 7570-86-7; **12**, 27729-98-2; **13**, 27729-99-3; **14**, 27730-00-3; **15**, 18873-05-7; **16**, 27730-02-5; **17**, 27730-03-6; **18**, 6531-10-8; **19**, 27730-05-8; **20**, 27730-06-9; **21**, 2211-61-2; **22**, 27730-08-1; **23**, 27730-09-2; **24**, 27730-10-5; **25**, 27730-11-6; **26**, 27730-12-7; **27**, 6372-30-1; **28**, 6450-55-1; **29**, 27730-15-0; **30**, 27730-16-1; **31**, 2211-65-6; **32**, 27730-18-3; **33**, 27730-19-4; **34**, 27730-20-7; **35**, 27730-12-8; **36**, 27730-22-9; **37**, 6667-81-8.

Chemistry of Enolates. VII. Kinetics and Orientation in Dimethyl Sulfoxide. Relative Nucleophilicities of Enolates[1]

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Lithium, sodium, and cesium enolates are prepared in dimethyl sulfoxide by titration of ketones with methylsulfinyl carbanion, $CH_3SOCH_2^-$. Rates of enolate alkylation in DMSO are 10^3-fold greater than in glyme solvents, and O-/C-alkylation ratios are substantially larger and more nearly independent of the cation. Carbon alkylation increases as the leaving group is varied from chloride to iodide. Enolate nucleophilicities calculated from the equation $\log k/k_0 = sn$ are obtained from partial rate constants for O- and C-alkylations by alkyl chlorides. Nucleophilicities increase with basicities of enolates as measured by pK_a values of the corresponding ketones.

The effect of dipolar aprotic solvents on the basicity and nucleophilicity of carbanions is an area of considerable recent interest.[2-9] Enhanced rates are explained by solvation of the accompanying cation[2-4] and by lack of solvation of the anion itself.[5] Of the common dipolar aprotic solvents, cation–solvent interactions are exceptionally strong in dimethyl sulfoxide.[2] Also, this solvent forms complexes with certain highly polarizable leaving groups such as iodide ion[10] and is effective in solvating extended, charged transition states, such as those encountered in SN2 and E2 mechanisms.[5-7] Finally, the strongly basic methylsulfinyl (dimsyl) carbanion, prepared in this solvent by the action of sodium hydride, provides a rapid quantitative conversion of weakly acidic compounds to their conjugate bases.[11]

In this solvent we find O-/C-alkylation ratios higher than in ethereal solvents and insensitive to variation of the cation. Also, improved bimolecular kinetics for the alkylation of sodium enolates are exhibited. Nucleophilicities of the anions are obtained from partial rate constants for O- and C-alkylation.

Results and Discussion

Sodium, lithium, and cesium enolates were prepared in DMSO by titration with dimsyl reagent to a triphenylmethane end point.[11] The success of this method depends on the relative acidities of DMSO, ketone, and indicator. The pK_a of DMSO is 31.3 compared with 27.3 for triphenylmethane. End points occurred when the calculated amounts of dimsyl reagent had been added to ketones with pK_a's in the range 16.1–20.3 (Table I). The quantitative conversions indicate the absence of condensation, for addition of enolate anion to another molecule of ketone would give rise to a premature end point. Glpc analysis of quenched aliquots eliminated the possibility of dimsyl addition to the carbonyl group; only the original ketones were recovered.

Alkylation of Sodium Enolates.—Second-order kinetics were observed for alkylations of sodium enolates by alkyl chlorides in DMSO. In Table II are listed second-order rate constants for the reactions of four sodium enolates with three alkyl chlorides. Figures 1 and 2 illustrate the second-order behavior and emphasize the rate dependence upon structure of enolate and alkylating agent.

Comparisons of alkylation rates in DMSO with those observed in ethereal solvents would be of interest. Unfortunately, most alkylations of sodium enolates in the ethers and glymes have been made with alkyl bromides and iodides and are too rapid in DMSO to be followed by conventional techniques. One comparison can be made. The rates of alkylation of sodiobutyrophenone by *n*-propyl chloride in monoglyme,[4] diglyme, and DMSO are 2×10^{-6}, 7×10^{-6}, and 7.6×10^{-3} sec^{-1} M^{-1}, respectively. Since diglyme is 5×10^3 times more effective than ethyl ether,[4] relative rates at 30° for alkylation in the four solvents are those given in parentheses: ether (1), monoglyme (10^2), diglyme (10^3), dimethyl sulfoxide (10^6).

(1) A grant from the National Science Foundation in support of this research is gratefully acknowledged.

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(5) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962); J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, **83**, 117 (1961); A. J. Parker, *J. Chem. Soc.*, 1328 (1961).

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(8) R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960); L. Friedman and H. Schechter, *ibid.*, **25**, 877 (1960).

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(10) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956); E. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

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TABLE I
CONVERSION OF KETONES TO ENOLATES BY DIMSYL REAGENT

Ketone	pK_a[b]	Equivalents of dimsyl ion needed for $(C_6H_5)_3C^-$ color[a] DmNa	DmLi	DmCs
Deoxybenzoin	16.1	1.04 ± 0.02		
Diphenylacetophenone	16.6		1.07 ± 0.00	
Butyrophenone	18.6	0.99 ± 0.01	1.02 ± 0.02	1.06
Acetophenone	19.1	1.08		
Isobutyrophenone	19.5	0.99 ± 0.03	1.08 ± 0.04	
Diethylacetophenone	20.3	0.96 ± 0.03		

[a] The red triphenylmethide end point was clearly observed and located to a single drop of dimsyl reagent. [b] Footnote 12.

TABLE II
ALKYLATION OF SODIUM ENOLATES IN DIMETHYL SULFOXIDE

$C_6H_5COCHRR'$ R	R'	pK_a	RCl	$[NaE]_0$, M	$[RCl]_0$, M	k_2 at 30°, sec^{-1} $M^{-1} \times 10^3$	Products, % O-Alkyl	C-Alkyl	Elimination	$k_O \times 10^3$	$k_C \times 10^3$
H	C_6H_5	16.1	*n*-Pr	0.144	0.463	0.64	21	79	0	0.13	0.51
			n-Am	0.112	0.513	0.60	22	78	0	0.13	0.47
			i-Bu	0.092	1.20	0.072	17	80	3	0.012	0.058
H	C_2H_5	18.6	*n*-Pr	0.159	0.368	7.58	56	43	1	4.2	3.3
			n-Am	0.123	0.535	6.16	53	44	3	3.3	2.7
			i-Bu	0.084	0.681	1.29	31	60	9	0.40	0.77
CH_3	CH_3	19.5	*n*-Pr	0.150	0.282	10.9	55	41	4	6.0	4.5
			n-Am	0.151	0.268	9.6	62	29	9	6.0	2.8
			i-Bu	0.126	0.638	1.88	32	47	21	0.60	0.88
C_2H_5	C_2H_5	20.3	*n*-Pr	0.130	0.197	11.5	84	12	4	9.7	1.4
			n-Am	0.167	0.553	7.65	86	9	5	6.6	0.69
			i-Bu	0.146	0.550	1.45	54	15	31	0.78	0.22

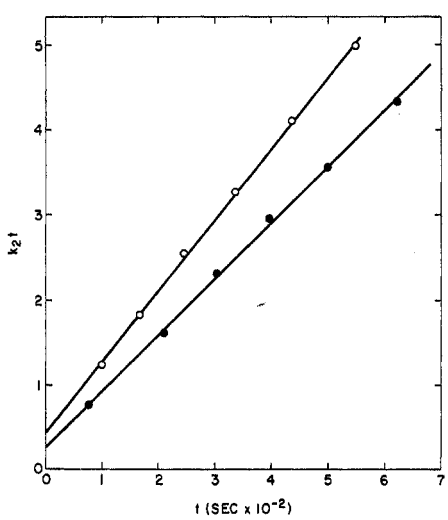


Figure 1.—Alkylation of sodioisobutyrophenone (○) and sodiobutyrophenone (●) by *n*-amyl chloride.

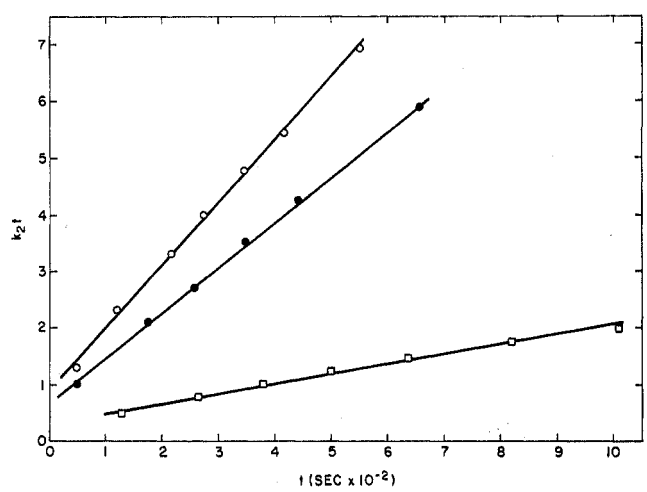


Figure 2.—Alkylation of sodiodiethylacetophenone by *n*-propyl (○), *n*-amyl (●), and isobutyl (□) chlorides.

A competing elimination reaction was appreciable only in alkylations by isobutyl chloride. In these, isobutylene was identified by glpc analyses, and the original ketone determined quantitatively along with the O- and C-alkylation products on infinity aliquots. The percentage of elimination increases tenfold with the basicity of enolates from ketones spanning a range of four pK_a units. A similar dependence on enolate basicity had been observed for dehydrohalogenation in glyme solvents.[12]

O/C Orientation.—Although O-alkylation is commonly observed with β-keto esters[13,14] and phenols,[3,15] few examples of enol ether formation from simple ketones have been reported.[4,9] These alkylations usually are carried out in media of low cation solvating power in which the cation is closely associated with the oxygen of the enolate. The effect of DMSO in promoting O-alkylation was demonstrated in the methylation of diphenylacetophenone by methyl iodide where the O/C ratio increased from 0.09 in diglyme to 1.0 in 50:50 diglyme–DMSO.[4] Enol ether is the major product in more than half of the alkylations listed in Table III. Comparisons of solvent effects must be made with care because, as shown in this table, O/C ratios are highly dependent on the structure of the enolate and the leaving group of the alkylating agent.

(12) H. D. Zook, W. L. Kelly, and I. Y. Posey, *J. Org. Chem.*, **33**, 3477 (1968).

(13) A. Brändström, *Ark. Kemi*, **6**, 155 (1954); **7**, 81 (1954); *Acta Chem. Scand.*, **7**, 223 (1953); A. Chatterjee, D. Banerjee, and S. Banerjee, *Tetrahedron Lett.*, No. 43, 3851 (1965).

(14) Similar results are reported for alkylations of acetoacetic ester in DMSO: W. J. le Noble and J. E. Puerta, *ibid.*, No. 10, 1087 (1966).

(15) D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Amer. Chem. Soc.*, **80**, 1391 (1958).

TABLE III
ORIENTATION OF ALKYLATION IN DMSO

$-C_6H_5C{=}CRR'-$ (O⁻)

R	R′	Registry no.	M⁺	O-/C-alkylation ratio at 30°: n-PrCl	i-BuCl	n-AmCl	n-AmBr	n-AmI
H	C_6H_5	17003-50-8	Na	0.27	0.21	0.28	0.14	
H	C_2H_5	27617-90-9	Li	1.1[a]	0.52	1.3	0.50[b]	0.20[c]
		17003-51-9	Na	1.3	0.52	1.2	0.64	0.23
		27557-74-0	Cs			1.3		
CH_3	CH_3	27557-75-1	Li		0.73	2.2		
		27557-76-2	Na	1.3	0.68	2.1		
C_2H_5	C_2H_5	27557-77-3	Na	7.1	3.6	9.2	[d]	
C_6H_5	C_6H_5	27557-78-4	Li	>100		>100		

[a] n-Propyl bromide gave O/C = 0.44. [b] At 50°, O/C = 0.67. [c] With ethyl iodide O/C = 0.13. [d] With ethyl bromide O/C = 1.9.

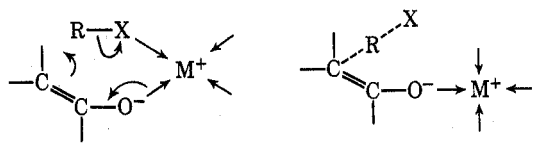
Nonetheless, O-alkylation is a major reaction yielding substantial amounts of enol ether in DMSO under mild conditions.

Perhaps the most surprising observation is the insensitivity of the O/C ratio to change of metal cation. The results might suggest that the reactant is the unencumbered carbanion set free by the cation-solvating power of DMSO. This view is reinforced by the large increase in molar conductance when DMSO is added to a dimethoxyethane solution of sodiobutyrophenone.[4] That the anion is not free is shown by the pronounced cation effect on the alkylation rate; *e.g.*, half-lives for the alkylations of 0.1 *M* sodio- and lithiobutyrophenone by 0.5 *M* *n*-amyl chloride are 2×10^2 and 6×10^4 sec, respectively. Thus, although it does not greatly influence O/C orientation, the solvated cation is important in the transition state.

The enolates in Table III are arranged in order of increasing steric hindrance to attack at the α-carbon atom. Without exception, all halides produce a higher O/C product ratio as crowding at the α position increases. Unexpectedly, the ratios for isobutyl chloride were found to be lower than those for *n*-propyl and *n*-amyl chlorides even with ketones with low pK_a where the competing elimination reaction is insignificant.

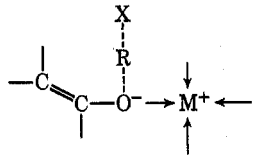
Finally, the nature of the leaving group appears to be the most important factor affecting the O/C product ratio. The percentage of O-alkyl product decreases markedly as halide is varied from Cl to Br to I.[14] The results are particularly surprising when compared with the high O/C ratios obtained when the leaving groups are sulfate and tosylate.[4]

Transition states I and II differ only in the ordering



I

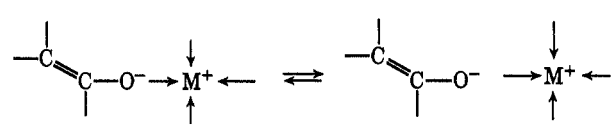
II



III

of halide and enolate. The cyclic transition state I has been suggested to explain the almost exclusive C-alkylation of β-dicarbonyl compounds[13] and the heterogeneous C-alkylation of phenols.[3] Linear geometry for the SN substitution is not essential; intramolecular alkylations of γ-bromopropylmalonic ester[16] and γ-chlorobutyronitrile[17] to cycloalkyl compounds are well known. Reaction within a solvated complex would provide a favorable entropy change for C-alkylation by the bulky isobutyl group, and the observed dependence of the O/C ratio on the leaving group is in accord with C–X bond polarizabilities. The lack of dependence of the O/C ratio on the cation, however, is not consistent with this hypothesis. Probably the greatest weakness in the argument for I is the absence of coordination compounds involving alkyl halides as ligands. Complex formation between ethyl bromide and sodiobutyrophenone could not be detected by vapor pressure measurements in ethyl ether, a less competitive solvent than DMSO.[18]

The 300-fold increase in rate from Li to Na enolate with essentially constant O/C ratio is difficult to explain in terms of transition states II and III, but rather suggests an alkylation of the free carbanion or solvent-separated ion pair in equilibrium with an ion pair or



higher aggregate. Conductances of ethereal enolate solutions are increased markedly by addition of DMSO.[4] The equilibrium position would be expected to vary with the change in cation, but the O/C ratio would be less sensitive to this change. On the other hand, some influence of the solvated cation is needed to explain the relatively lower amounts of O-alkylation by isobutyl chloride and alkyl iodides.[19]

Relative Nucleophilicity.—The lack of solvation of anions by DMSO suggests that the simplified form of the Swain–Scott equation,[21] $\log k/k_0 = sn$, might correlate nucleophilicities (n) of enolate ions and susceptibilities (s) of alkylating agents to nucleophilic substi-

(16) G. B. Heisig and F. H. Stodola, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 213.
(17) M. J. Schlatter, ref 16, p 223.
(18) H. D. Zook and W. L. Gumby, *J. Amer. Chem. Soc.*, **82**, 1386 (1960).
(19) The authors are indebted to a reviewer for pointing out a possible application of the Hammond postulate[20] to this situation. The transition states for chloride displacements will be more productlike than those for iodide displacements, and, when the leaving Cl^- is closer to M^+ (III), the barrier will be relatively lower. The bulk of the solvated cation may cause the greater sensitivity of O-alkylation to steric hindrance in the alkylating agent.
(20) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).
(21) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

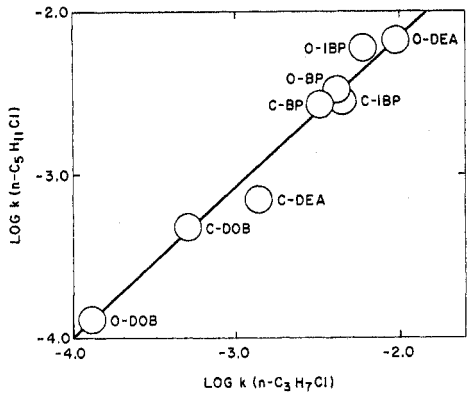


Figure 3.—Swain–Scott comparison of O- and C-alkylations by *n*-propyl and *n*-amyl chlorides: DOB = deoxybenzoin, DEA = diethylacetophenone, BP = butyrophenone, IBP = isobutyrophenone.

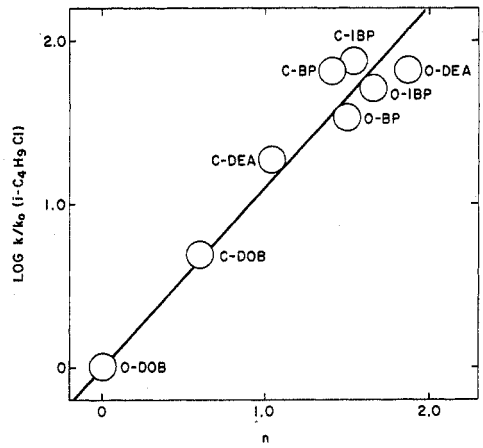


Figure 4.—Swain–Scott plot for alkylations by isobutyl chloride.

tution. Furthermore, from the partial rates of O- and C-alkylation, relative nucleophilicities for the two sites of an ambident ion could be determined. Partial rates k_O and k_C for the several alkylations are listed in Table II, and a comparison of two halides is shown in Figure 3. Good linearity was obtained except for carbon alkylation of the most hindered ketone diethylacetophenone. By choosing as reference parameters $s = 1$ for *n*-propyl chloride and k_0 = the partial specific rate for the formation of *O*-alkyldeoxybenzoin, the nucleophilic constants listed in Table IV were obtained.

TABLE IV
NUCLEOPHILIC CONSTANTS

Nucleophile	*n*	Nucleophile	*n*
O-DOB	0.00	O-BP	1.51
C-DOB	0.60	C-IBP	1.54
C-DEA	1.04	O-IBP	1.67
C-BP	1.41	O-DEA	1.88

Finally, alkylations by isobutyl chloride are correlated with *n* in Figure 4. Susceptibility constants (*s*) for *n*-amyl chloride and isobutyl chloride are 0.94 and 0.96, respectively.

The low nucleophilicity of diethylacetophenone enolate to C-alkylation suggests hindrance at this position by the two ethyl groups, whereas the high value for O-alkylation is in accord with the high pK_a of this ketone. Low values for deoxybenzoin enolate are in line with its low basicity and reflect the stabilization of this enolate by resonance involving the phenyl group. Unfortunately, a comparison of enolate nucleophilicities with those of the ions studied by Swain and Scott will have to await more extensive kinetic studies of SN2 reactions in DMSO.

Experimental Section

Materials.—Dimethyl sulfoxide was dried by distillation from dimsyllithium solution. Approximately 100 ml of the solvent containing a few crystals of triphenylmethane was treated with 50 ml of *n*-butyllithium in hexane (Foote Mineral Co.). The red tritryllithium–dimsyllithium solution was separated by means of a syringe from the hexane layer and added to a stirred solution of 2.5 l. of dimethyl sulfoxide containing triphenylmethane until a permanent red color was produced. An additional 50 ml was then added and the solution distilled at 1 mm through a 90-cm column packed with stainless steel helices. The first 50 ml of distillate was discarded and the remainder stored under a positive pressure of nitrogen.

Alkyl halides (Eastman Kodak Co.) were analyzed on a 20-ft column of diethylene glycol succinate on Chromosorb. All were of acceptable purity except isobutyl chloride which required fractional distillation from dry potassium carbonate through an 18-plate column packed with glass helices. The fraction boiling at 64.5° (738 mm) gave a single peak by glpc analysis.

The preparations of ketones have been described.[4] Purity was checked by glpc analysis on a 5 ft × 0.3 mm column of phenylsilicone on Gas Chrom Z.

Apparatus.—Vacuum-line techniques were used for the preparation, storage, and transfer of dimsyl and enolate solutions. The manifold provided for nitrogen inlets, mercury manometers, and a 2-l. preparation and storage flask equipped with a magnetic stirrer and fritted glass filter through which the dimsyl solution could be siphoned to a 100-ml buret. The buret was connected to a 200-ml reaction flask which carried a mercury-sealed stirrer and 12.4-ml automatic sampling buret. A constant temperature bath mounted on a jack could be lowered to permit removal of the reaction flask. Kinetic measurements were made at 30.00 ± 0.05°. The apparatus was washed with dry pentane and evacuated under an infrared lamp for 24 hr prior to use.

Dimsyl Reagents (Caution).[22]—The sodium compound[11] was prepared from 1700 ml of dry dimethyl sulfoxide and 10 g of 50% sodium hydride dispersion (Metal Hydrides, Inc.) from which the oil was extracted by three 100-ml portions of pentane. Hydrogen evolution proceeded at a moderate rate for 12 hr. The clear, yellow solution was degassed under vacuum and stored under positive nitrogen pressure protected from light by aluminum foil. The lithium compound was made from 1700 ml of dimethyl sulfoxide and 130 ml of *n*-butyllithium in hexane. A clear, orange solution resulted after evolution of butane, distillation of the insoluble hexane, and vacuum degassing.

Kinetic and Product Studies.—The reaction flask was flamed and cooled under nitrogen. Enolate solutions were made by titrating weighed amounts of ketone with about 100 ml of dimsyl reagent to a triphenylmethane end point. After the addition of alkyl halide, samples were periodically quenched in water and titrated with standard acid to a phenolphthalein end point. For product analysis, infinity samples were quenched in 0.1 *M* sodium hydroxide solution and extracted twice with 5-ml portions of carbon tetrachloride. Infrared spectra were measured in a 1-mm cell on a Beckman IR-8 spectrometer. O-Alkylation was detected by broad peaks near 1063 cm^{-1}, the region for vinyl ether stretching and C-alkylation by sharp peaks near 1675 cm^{-1}, the carbonyl stretching region. A second sample of the carbon tetrachloride extract was shaken with 5 ml of hydrochloric acid, and the analysis repeated. Absorption at 1063 cm^{-1} disappeared and that in the carbonyl region increased. Quantitative analyses of the extracts were performed on a Perkin-Elmer 154 D vapor fractometer using a 5 ft × 0.3 mm column packed with GE SF-96 (phenylsilicone) on 100–140 mesh Gas Chrom Z. The above column, when operated at temperatures ranging from 150 to 200°

(22) F. A. French, *Chem. Eng. News*, **44** (15), 48 (1966).

and a flow rate of 50 ml of helium per minute satisfactorily separated all components of most alkylation mixtures. In the cases of poor separation, a 2-m Ucon 50 column was an excellent substitute. A second sample was subjected to acid hydrolysis. The peak that disappeared was *O*-alkyl product, that which increased, starting ketone, and that which remained constant, *C*-alkyl material. A chromatographic analysis on the original reaction mixture before quenching showed that equal partitioning of O and C product had occurred during extraction. Glpc products from the alkylation of sodiobutyrophenone by isobutyl chloride were trapped in liquid nitrogen, dissolved separately in carbon tetrachloride, and rechromatographed. No degradation of products or isomerization of enol ether could be detected.

Cesiobutyrophenone.—To 1.8 g (8.0×10^{-3} mol) of cesium graphite (Callery Chemical Co.) and a few crystals of triphenylmethane in the reaction flask was added 100 ml of dry dimethyl sulfoxide. Immediate evolution of heat and precipitation of carbon occurred. The clear, red solution from which the carbon had settled upon standing was treated with 1.0 ml (6.6×10^{-3} mol) of butyrophenone and 5.0 ml (4.13×10^{-2} mol) of *n*-amyl chloride. After stirring for 3 hr the solution was filtered and analyzed as described above.

The Action of Sulfuric Acid on Ethyl 3,3-Diphenyl-3-hydroxypropanoate

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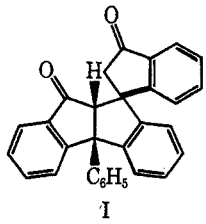
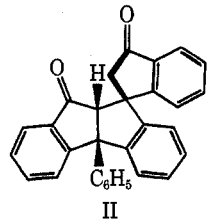
The reaction of sulfuric acid with ethyl 3,3-diphenyl-3-hydroxypropanoate gave *cis*- and *trans*-spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one]. The structures were based on spectral data and chemical reactions. Pyrolysis of the monobromo derivatives gave benz[*a*]indeno[1,2-*c*]fluorene-9,14-dione and 7b,12-dihydro-7b-phenyldibenz[*cd*,*f*]indeno[2,1-*a*]azulene-12,14-dione. The former compound was also obtained by treating the trans isomer with aluminum chloride in nitrobenzene and was synthesized from benzo[*c*]fluorene.

The unusual dimerization observed in attempts to prepare 2-phenylindenone[3] suggested a study of the structures of the products obtained by the action of sulfuric acid on ethyl 3,3-diphenyl-3-hydroxypropanoate. These products have been formulated as dimers of 3-phenylindenone involving cyclobutane rings.[4-6]

In agreement with these investigations, the action of sulfuric acid on ethyl 3,3-diphenyl-3-hydroxypropanoate gave isomeric ketones melting at 255–259° (I) and 224–226° (II). The nmr spectra of these two compounds were not in agreement with the truxone structures postulated.[4,5] Isomer I gave a singlet at δ 3.88 (1 H), half of an AB quartet at δ 3.84 (J = 19 cps) (1 H), and the other half at δ 2.58 (J = 19 cps) (1 H). Isomer II showed a singlet at δ 3.51 (1 H) and a singlet at δ 3.08 (2 H). These spectra, together with the ir and mass spectral data, are better accommodated by formulation of these compounds as *trans*- and *cis*-spiro[indan-1-one-3,10′-[4b,9a]dihydro-4b-phenylindeno[1,2-*a*]inden-9-one] (I, II).[7]



I

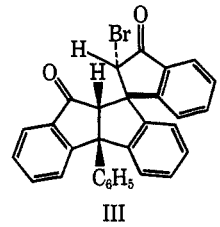


II

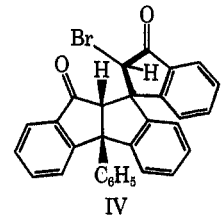
In II the methylene hydrogens are in a similar magnetic environment and appear, fortuitously, as a singlet. The environments of these two protons in isomer I are different since one of the methylene hydrogens is deshielded by the carbonyl grouping and an AB quartet is therefore observed.

Further evidence for these structures is derived from chemical behavior of the two isomeric diketones and the spectra of the products formed. In agreement with the spiran structure, isomer I was stable to chloranil and dichlorodicyanoquinone in refluxing benzene. Treatment with palladium on carbon in boiling cymene and at 250–260° effected no dehydrogenation.

The trans isomer I when treated with bromine in acetic acid gave a monobromo derivative which showed nmr spectral properties consistent with structure III.



III



IV

The 2 hydrogen appeared at δ 6.10 ppm and the 9a hydrogen (δ 3.83 ppm) showed very little change from its value in the parent compound I. The large downfield shift observed for the 2 hydrogen suggests that deshielding occurs both by the carbonyl group and the bromine atom. The structure III shown would result from the expected attack of the bromine on the less hindered side of the methylene carbon.

Cis isomer II formed a monobromo (IV) and a *gem*-dibromo compound. The nmr spectrum for IV indicates that the 2-bromo substituent must be on the same side as the 9a hydrogen since the relative shifts for the 9a hydrogen resulting from the consecutive introduction of bromine atoms is larger for the first bromine atom (0.70 ppm) than for the second (0.24 ppm). The reason for the preferential attack by the bromine may be steric.

Dehydrohalogenation of the monobromo products could only be accomplished by pyrolysis and led to the rearranged products, benz[*a*]indeno[1,2-*c*]fluorene-9,-

(1) To whom inquiries should be addressed.

(2) Abstracted in part from the Ph.D. Thesis of N. A. R., May 1970.

(3) S. Wawzonek, G. R. Hansen, and Z. R. Zigman, *Chem. Commun.*, 6 (1969).

(4) F. DeFazi, *Gazz. Chim. Ital.*, **49**, 253 (1919).

(5) R. Stoermer and G. Foerster, *Chem. Ber.*, **52**, 1255 (1919).

(6) B. W. Rockett and C. H. Hauser, *J. Org. Chem.*, **29**, 1394 (1964).

(7) Cis and trans refer to the relationship of the hydrogen at C-9a, and the methylene group at spiro C-10.