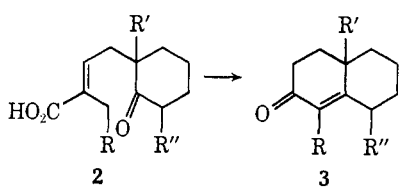


requires no protection of the existing ketone and is compatible with acid-sensitive functionality. Typically, yields for the conversion of unsaturated acids **2** to *N*-vinyl carbamates, **4**, were greater than 90% overall; spectral properties of the oily intermediates were consistent, in each case, with the structures anticipated.

Final "unmasking" of the newly introduced 3'-ketoalkyl substituent was effected *via* 2% KOH in 4:1 methanol-water for 1 hr at 25° then 2 hr at 70°, thus allowing for direct cyclization of the intermediate δ -diketones to annelated products **3** in high yield (usually about 90%). These conditions, which are essential for cyclodehydration in any "Robinson annelation," are the most drastic in this "unmasking" sequence.

Table II describes yields of distilled enones **3** derived from keto-unsaturated acids **2**. All annelation products

Table II. Representative Examples and Yields for the Conversion of Acids, **2**, to Annelated Products, **3**



	Mp, °C	% of 3 distilled yield (based on 2)	Reference to comparison data for 3 and deriva- tives
2a , R' = CH ₃ ; R = R'' = H	98-100	80	2a
2a , R = R' = CH ₃ ; R'' = H	103-104	85	<i>a</i>
2b , R = R' = H; R'' = CH ₃	106-108	83	2a , 2b
2c , R = R' = R'' = H	85.5-86.5	82	2b
2c , R = CH ₃ ; R' = R'' = H	63-68	81	<i>b</i>

^a F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); F. J. McQuillin, *ibid.*, 528 (1955). ^b Y. Kawase, *Bull. Chem. Soc. Jap.*, **31**, 336 (1958).

3 were identified by comparison of their physical and spectral properties as well as those of their solid 2,4-dinitrophenyl hydrazones with data previously reported. In each case, the annelations were position-specific and no structural isomers were observed.

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Carbonyl $n \rightarrow \pi^*$ Solvent Blue Shift. Excited State Solvation *vs.* Ground State Solvation

Sir:

The well-known blue shift of the $n \rightarrow \pi^*$ transition of carbonyl compounds on going to more polar solvents can be attributed to superior solvation of the polar ground state by the polar solvent¹ or to inferior solvation of the excited state by the polar solvent.² The following evidence shows that, in the case of acetone, solvation of the ground state accounts for only about a half of the above phenomenon, the other half being caused by desolvation of the excited state³ in the polar solvent. Figure 1 illustrates this fact for the $n \rightarrow \pi^*$ transition of acetone in CCl₄ and H₂O solvents, using λ_{\max} values for the acetone $n \rightarrow \pi^*$ transition in these two solvents of 280.1⁴ and 264.9 nm,⁵ respectively, and heats of solution of acetone in the two solvents of 0.79⁶ and -2.37 kcal/mol,⁷ respectively. As can be seen, the CCl₄-H₂O solvent shift of 15.2 nm or 5.86 kcal/mol is caused by a 3.16 kcal/mol exothermic enthalpy of transfer of the acetone ground state ($\delta\Delta H_s$) and a 2.70 kcal/mol endothermic enthalpy of transfer of the excited state ($\delta\Delta H^*$) into the more polar solvent.⁸

To see whether this conclusion holds generally we can next examine the behavior of benzophenone in a more extensive series of solvents. The necessary heats of solution were measured and are shown in Table I. From these, and the data of Ito,⁴ *et al.*, the enthalpies of solvent transfer of the excited states were calculated and are tabulated in Table II and shown graphically in Figure 2.

The most general conclusion that can be drawn is that changes in solvation of the excited state of benzophenone contribute significantly to the magnitude of the solvent blue shift. Thus, the large blue shift on going from hexane to ethanol or acetonitrile is clearly due to the same kind of cooperative effect which causes the acetone blue shift on going from CCl₄ to H₂O solvent (*cf.* Figures 1 and 2), *i.e.*, increased ground state solvation accompanied by diminished excited state solvation on going to the more polar solvent. On the other hand the other four solvents examined (methyl acetate, carbon

(1) *E.g.*, G. J. Brealey and M. Kasha, *J. Amer. Chem. Soc.*, **77**, 4462 (1955); M. P. sterner and D. Brück in "Methoden der Organischen Chemie: (Houben-Weyl)," Vol. III, part II, E. Müller, Ed., G. Thieme Verlag, Stuttgart, 1955, p 738; G. C. Pimentel, *J. Amer. Chem. Soc.*, **79**, 3323 (1957); S. F. Mason, *Quart. Rev., Chem. Soc.*, **15**, 287 (1961); S. K. Freeman, "Interpretive Spectroscopy," Reinhold, New York, N. Y., 1965, p 31; H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, p 99; E. F. H. Brittain, W. O. George, and C. H. J. Wells, "Introduction to Molecular Spectroscopy," Academic Press, New York, N. Y., 1970, p 46.

(2) *E.g.*, R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley, New York, N. Y., 1969, p 37; N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, 1970, p 399.

(3) The excited state referred to here is, of course, not the "equilibrium" excited state after vibrational and solvent relaxation. The Franck-Condon principle requires that the observed electronic transition be to an excited state having a geometry and solvent shell geometry identical with that of the ground state. It is to this Franck-Condon excited state that our discussion pertains.

(4) M. Ito, K. Inuzuki, and S. Imanishi, *J. Amer. Chem. Soc.*, **82**, 1317 (1960).

(5) P. Maroni, *Ann. Chim. (Paris)*, **13**, 757 (1957); J. E. Dubois, E. Goetz, and A. Bienvenue, *Spectrochim. Acta*, **20**, 1815 (1964).

(6) J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 5136 (1970).

(7) E. M. Arnett, *J. Amer. Chem. Soc.*, **88**, 2598 (1966).

(8) $\delta\Delta H^* = \delta\Delta H_s + \delta\Delta E^{n \rightarrow \pi^*}$ where $\delta\Delta E^{n \rightarrow \pi^*}$ is the solvent blue shift in kcal/mol.

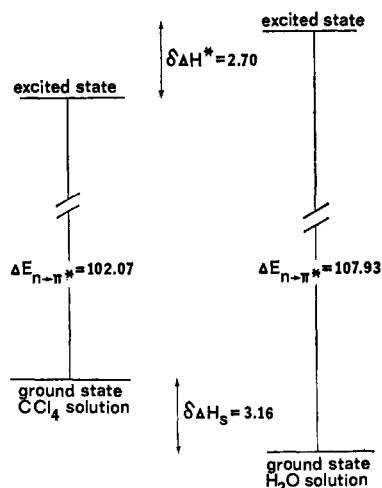


Figure 1. Relative energies (kcal/mol) of the ground states and the excited states of the $n \rightarrow \pi^*$ transition of acetone in CCl_4 and H_2O solvent.

Table I. Heats of Solution (ΔH_s) of Benzophenone and Enthalpies of Transfer of Benzophenone from Hexane to Other Solvents ($\delta\Delta H_{\text{ground state}}$ (hexane \rightarrow solvent)) in kcal/mol

Solvent	Dielectric constant ^a	Dipole moment, ^b D	ΔH_s^c	$\delta\Delta H_{\text{ground state}}$ (hexane \rightarrow solvent)
Hexane	1.9	0.0	6.53	0.00
Carbon tetrachloride	2.2	0.0	4.54	-1.99
Benzene	2.3	0.0	4.18	-2.35
Methyl acetate	7.3	1.7	4.59	-1.94
Acetonitrile	3.9	3.4	5.31	-1.22
Chloroform	4.9	1.1	2.45	-4.08
Ethanol	25.7	2.9	5.56	-0.97

^a From C. Marsden and S. Mann, "Solvents Guide," Interscience, New York, N. Y., 1963. ^b From A. L. McClellan, "Tables of Experimental Dipole Moments," W. M. Freeman, San Francisco, Calif., 1963. ^c Molar heat of solution (integral), measured using an LKB 8700 calorimeter, benzophenone concentration 0.006–0.03 M, all values better than ± 0.1 kcal/mol.

Table II. The Solvent Blue Shift ($\delta\Delta E_{n \rightarrow \pi^*}$ (hexane \rightarrow solvent)) and the Energy of Transfer of the Benzophenone $n \rightarrow \pi^*$ Excited State from Hexane to Other Solvents ($\delta\Delta H_{\text{excited state}}$ (hexane \rightarrow solvent)) in kcal/mol^a

Solvent	$\lambda_{\text{max}},^b$ nm	$\delta\Delta E_{n \rightarrow \pi^*}$ (hexane \rightarrow solvent)	$\delta\Delta H_{\text{excited state}}$ (hexane \rightarrow solvent)
Hexane	347.10	0.00	0.00
Carbon tetrachloride	344.11	0.72	-1.27
Benzene	343.05	0.97	-1.38
Methyl acetate	342.11	1.20	-0.74
Acetonitrile	338.87	2.00	0.78
Chloroform	333.70	2.46	-1.62
Ethanol	333.11	3.46	2.49

^a $\delta\Delta H_{\text{excited state}}$ (hexane \rightarrow solvent) = $\delta\Delta H_{\text{ground state}}$ (hexane \rightarrow solvent) + $\delta\Delta E_{n \rightarrow \pi^*}$ (hexane \rightarrow solvent). ^b From ref 4.

tetrachloride, benzene and chloroform) exhibit a similar solvent effect on the ground state and on the excited state, with the effect on the latter being somewhat damped in each case. This similarity in solvation of the ground and excited states has the effect of diminishing the magnitude of the solvent blue shift in these cases. It should be noted that the greatest solvent blue shift, here as in other examples of the $n \rightarrow \pi^*$ transition, is

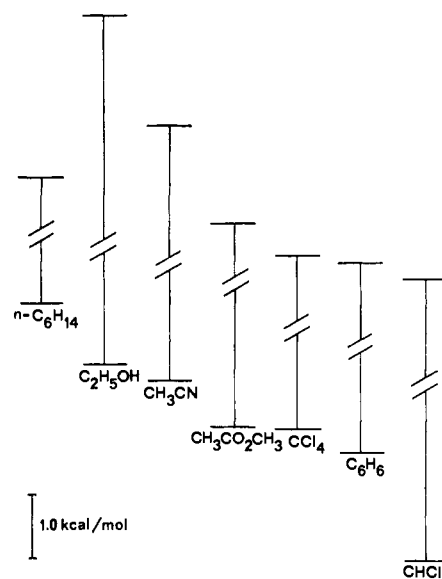


Figure 2. Relative energies of the ground states and the excited states of the $n \rightarrow \pi^*$ transition of benzophenone in seven solvents.

observed for the H bonding solvent (ethanol); however, contrary to accepted views, this is clearly *not a ground state effect*. The effect on the excited state (2.49 kcal/mol) is 2.5 times greater than the effect on the ground state (-0.97 kcal/mol), the solvent effect on the excited state thus making the major contribution to the blue shift. On the other hand chloroform solvent, which exhibits by far the greatest degree of ground state solvation and should, therefore, on the basis of accepted reasoning, produce by far the greatest solvent blue shift, has in fact a blue shift which is considerably smaller than that produced by ethanol.

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Dehalogenations with Sodium Borohydride. Evidence for a Free Radical Reaction

Sir:

Reduction of alkyl and aryl halides with sodium borohydride is well known and has been reported, variously, to proceed *via* an $\text{S}_{\text{N}}1$ process,¹ an $\text{S}_{\text{N}}2$ process, or nucleophilic attack on halogen² depending on the structure of the halide. Only recently has evidence appeared suggesting dehalogenation by a free radical path.³ In the course of our recent examination of the reaction of α -bromocyclopropyl trifluoroacetates⁴ with hydride reagents to afford cyclopropanols,⁵ it became apparent that *gem*-dibromocyclopropanes are appreciably reactive toward sodium borohydride as well, affording high yields of the corresponding mono-

(1) H. B. Bell and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 1473 (1966).

(2) H. M. Bell, C. W. Vanderslice, and A. Spehar, *J. Org. Chem.*, **34**, 3923 (1969).

(3) The photoreduction of iodobenzene in the presence of sodium borohydride proceeds with quantum yields in excess of unity; J. A. Bartrop and D. Bradbury, *J. Amer. Chem. Soc.*, **95**, 5085 (1973).

(4) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 5225 (1973).

(5) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974).