and 7.65 (4 H, A_2B_2 quartet, $J = 9$ cps, aromatic ring with NH_2), and multiplet between 6.84 and 7.50 (4 H aromatic ring with OCH_3).

Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.90; H, 5.77; N, 6.16. Found: C, 74.11; H, 5.76; N, 6.45.

Registry No.—II, 835-11-0; III, 606-12-2; V, 13134-93-5; VI, 13134-94-6; VIII, 1424-76-6; IX, 13134-96-8.

Heterogeneous Photosensitization

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Received March 14, 1967

The majority of photosensitized chemical reactions are conducted with the sensitizer and the substrate in the same physical phase and cross-phase sensitization is rarely used. However, use of a sensitizer in a different phase from that of the substrate has the advantage that there are no problems of separation of the sensitizer from the products or reactants. Practically, a suitable solid sensitizer could be placed in a column irradiated by a suitable light source, gaseous or liquid reactant run slowly over the sensitizer, and the reaction products eluted from the bottom of the column.

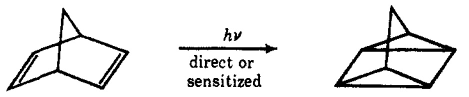
We have used the solid polymer polyvinylphenyl ketone (polyacrylophenone), the photosensitizing properties of which have been briefly investigated previously,[1] as a photosensitizer for the systems piperylene, norbornadiene, and myrcene.

Polyvinylphenyl ketone is closely analogous to acetophenone which is commonly used as a photosensitizer. Acetophenone has a triplet energy of 74 kcal/mole[2] and an intersystem crossover efficiency of 0.99.[3] A polymer with properties similar to these would be an efficient sensitizer of the three systems investigated.

Phenyl vinyl ketone was prepared as a pale yellow oil from β-chloropropionyl chloride.[4,5] Polymerization was effected by azobisisobutyronitrile initiation at 55° in benzene. The polymer was obtained as a plastic mass by precipitation from benzene by petroleum ether (bp 60°) and became quite brittle when vacuum dried. It was cut into small pieces (~2 mm^3) for sensitization experiments. The ultraviolet spectrum shows absorption at 280 mμ associated with the $n-\pi^*$ transition of the carbonyl group and the infrared spectrum shows the absorption at 1675 cm^{-1} characteristic of an aromatic carbonyl. The emission spectrum in an ether–tetrahydrofuran glass at 77°K showed a well-resolved progression of bands with maxima at 395 (0–0 band, triplet energy of 72.4 kcal), 420, 450, and 485 mμ, which compares to acetophenone under the same conditions with peaks at 380 (0–0 band, 74.0 kcal), 412, 440, and 472 mμ. Clearly the triplet state of the polymer is much like that of acetophenone.

Initially the polymer was used to sensitize the *cis–trans* isomerization of a 1.0 *M* solution of *cis*-piperylene in Spectrograde isopentane, a solvent in which the polymer was shown to be totally insoluble (to the limits of ultraviolet detection in the 280–320-mμ region). All energy transfer, then, must be heterogeneous. Typically, a well-stoppered test tube containing 0.3 g of the solid polymer and 2 ml of an isopentane solution of piperylene was attached to and irradiated by a water-cooled Hanovia 450-w medium-pressure reactor fitted with a Pyrex envelope to prevent direct excitation of the diene. A photostationary state *trans/cis* of 1.18 was obtained after 24 hr irradiation. This ratio is in the range expected from a sensitizer with a triplet energy close to that of acetophenone.[6]

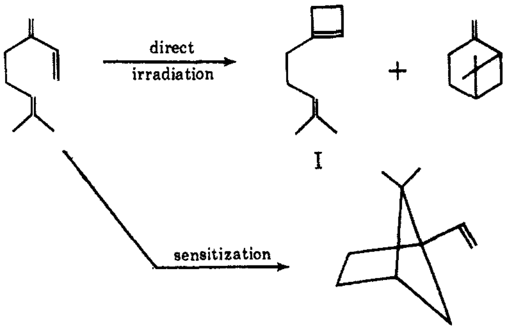
The valence isomerization of norbornadiene to quadricyclene (eq 1) has been found to be a quite clean reaction either by direct irradiation[7] or by sensitization with a variety of sensitizers.[8] A yield of 90% quadricyclene has been obtained with acetophenone as sensitizer in isopentane solution.[8]



(1)

Sensitization of neat norbornadiene by the polymer over a period of 17 hr gave a net yield (by vpc) of approximately 60% quadricyclene and a number of minor products. The conversion was kept to less than 10%. Identification of the quadricyclene was on the basis of comparison of its retention times with an authentic sample on vpc columns of S.E. 30 and S.F. 96 and its nmr spectrum. The nmr shows a broad group with its highest peak at τ 8.58 owing to the protons on the cyclopropane rings and a triplet owing to the methylene protons at τ 8.04.[7] During irradiation the polymer changed its form from solid pieces to a single plastic mass; however, a neat aliquot of supernatent liquid showed negligible absorption in the 300–320-mμ region indicating virtually no dissolution of the polymer.

The direct photolysis of myrcene produces a number of products of which 54% is the cyclobutene I and 9% is β-pinene.[9] In contrast, the sensitized photolysis produces just one product, 5,5-dimethyl-1-vinylbicyclo[2.1.1]hexane, with a quantum yield of 0.05[10] (eq 2).



(2)

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The polymer sensitization of neat myrcene over a 17-hr period gave a yield of 20% of the bicyclohexane. Identification was based on the nmr spectrum which showed singlets at τ 8.9 and 9.26, a doublet at τ 9.07, and a broad group around τ 5.05 associated with the vinyl protons.[10] The sensitizing polymer retained its solid granular form during irradiation.

Quite obviously many other systems would be amenable to this type of sensitization and variation of form and type of polymer would provide a wealth of information to supplement that already gained from homogeneous sensitization. We have selected a very limited set of conditions and systems, but obvious engineering and chemical refinements should permit broad usage of this technique.

Registry No.—Polyvinylphenyl ketone, 768-03-6.

Acknowledgment.—The authors are indebted to Drs. Harold Cassidy and Robert Moser for helpful discussion and to the National Institutes of Health (Grant GM13592-01) and the ACS Petroleum Research Fund for financial support.

Symbiotic Effects in Nucleophilic Displacement Reactions on Carbon

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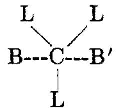
Received February 2, 1967

Inasmuch as the transition state for an SN2 reaction may be regarded as an acid–base complex, there should be symbiotic effects on the rates of nucleophilic displacement reactions;[2] that is, a grouping of either several hard[3] bases or several soft[3] bases around the central carbon atom should stabilize the transition state and cause an increased rate of reaction. The bases include the entering and leaving groups, B and B′, as well as the three groups, L, in the trigonal plane of the activated complex



Such an effect has been pointed out by Bunnett,[4] although there has been some dispute.[5] If we concentrate on the entering and leaving groups to minimize the effects of steric hindrance, then there is no doubt that symbiosis is important and dominates the so-called leaving-group effect. It is necessary, of course, to examine rates in a fixed solvent. A comparison of the relative rates of reaction of alkyl tosylates with alkyl iodides provides the clearest example. The tosylate group is very hard, being an oxygen donor, whereas the iodide ion is quite soft. Consequently tosylates should react rapidly with hard bases and iodides should react rapidly with soft bases. Much data in the literature show that this prediction is verified when applied to bromides rather than iodides.[6]

Table I shows rate constants which we have obtained for reaction 1 in methanol at 25°. These data may

$$B + CH_3OTs \longrightarrow CH_3B + OTs^- \qquad (1)$$

be compared with the corresponding rate constants for reaction with CH_3I in the same solvent and at the same temperature.[7] The ratios k_{TsO}/k_I strikingly confirm the prediction in that the ratio is large for hard nucleophiles, *e.g.*, OCH_3^-, CH_3OH, $(C_2H_5)_3N$, and Cl^-, and small for soft nucleophiles, *e.g.*, $C_6H_5S^-$, I^-, $SeCN^-$, and $(C_6H_5)_3P$. In the same way we find that the relative reactivities of RCl, RBr, and RI are functions of the softness of the nucleophile with which they react. The often-quoted[8] ratios of 1:50:100 are valid for alcohol, alkoxide ion, and amines in alcoholic solvents. When soft nucleophiles are used, the ratios become much higher in the same solvents.[9]

TABLE I

RATE CONSTANTS AT 25° IN METHANOL FOR THE REACTION $B + CH_3OTs \longrightarrow CH_3B + TsO^-$

Nucleophile B	k, M^{-1} sec^{-1}	k_{TsO}/k_I
$C_6H_5S^-$	1.42×10^{-1}	0.13
$SeCN^-$	2.15×10^{-3}	0.23
CH_3O^-	1.16×10^{-3} [a]	4.6
$CS(NH_2)_2$	5.60×10^{-4}	0.23
I^-	4.42×10^{-4}	0.13
$(C_6H_5)_3P$	2.3×10^{-4}	0.18
SCN^-	1.59×10^{-4} [b]	0.28
$(C_2H_5)_3N$	5.65×10^{-4}	0.95
Br^-	5.75×10^{-5}	0.72
Cl^-	8.5×10^{-6}	2.8
CH_3OH	2.50×10^{-8} [c]	210

[a] A value of 1.17×10^{-3} is given in E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964, p 164. [b] Rate constants for SCN^-, N_3^-, OH^-, and $S_2O_3^{2-}$ in water are given by R. E. Davis, *J. Am. Chem. Soc.*, **87**, 3011 (1965). [c] Calculated as a second-order reaction by dividing by 27. The first-order constant of 6.6×10^{-6} sec^{-1} agrees with that of R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

The symbiotic effect is useful in understanding the behavior of ambident nucleophiles as a function of the leaving group. Typically an ambident base, such as an enolate anion, has a softer nucleophilic center (the carbon atom) and a harder center (the oxygen atom). We expect alkyl sulfates and tosylates to react with enolate ions to give largely O alkylation,[10] whereas bromides and iodides react to give largely C alkylation.[11] It is also well known that the percentage of C alkylation *vs.* O alkylation rises steadily as one changes

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