from chrysene (5 × 10^{-4} *M*) and pyrene (5 × 10^{-5} *M*) with dimethyl fumarate (0.1 *M*) in benzene. In other related studies of reactions of aromatic hydrocarbons with olefins, no new emission band was observed in the phenanthrene–*trans*-methyl cinnamate system even at high enough concentrations of the cinnamate to drastically suppress the phenanthrene fluorescence. An exciplex emission was observed, however, in the pyrene–*trans*-cinnamonitrile system in benzene.

(10) Exciplex emissions from the reaction of a number of aromatic hydrocarbons with fumaronitrile were recently reported [Y. Shirota, I. Tsushi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **47**, 991 (1974)].

(11) M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973), and references therein.

(12) For a discussion of the triplet energies of dienes, cf. R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 3406 (1965).

(13) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(14) At high diene concentrations, quenching of the singlet exciplex[5] is detectable. The decrease of the cyclobutane–oxetane ratio is, however, a measure for the triplet quenching as shown in eq 4 in the Kinetics section.

(15) The ratio of *T/C from the triplet reaction*[3,4] is *1.9. The amount* of (*T* − 1.9C) will, therefore, give the amount of [T] formed via the stereospecific singlet pathway.

(16) On using F as a quencher for the benzophenone sensitized trans → cis isomerization of stilbene, it was found that the reaction constant for quenching benzophenone triplet (B^{*3}) by *F* is *0.45 times the reaction* constant for energy transfer from B^{*3} to stilbene. The latter reaction constant is assumed to be equal to that of energy transfer from B^{*3} to P.

(17) The Stern–Volmer slope for the fluorescence quenching of phenanthrene with dimethyl fumarate in degassed benzene was 595 l. mol^{-1} and in aerated benzene was 144. From the reported lifetime of P^{*1} in degassed and aerated solutions,[18] values of 10^{10} and 8.5 × 10^9 mol^{-1} sec^{-1} were obtained for k_4. Caldwell[4] reported a value of 7.5 × 10^9 for this reaction constant.

(18) The reported lifetime of P^{*1} at room temperature in degassed cyclohexane and benzene ranges between 55 and 57 nsec [C. D. Amata, M. Burton, W. P. Helman, P. K. Ludwig, and S. A. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1966); F. D. Lewis and J. C. Dalton, *J. Am. Chem. Soc.*, **91**, 5260 (1969); I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1965]. In aerated cyclohexane, a value of 17 nsec is reported (F. Wilkinson, "Fluorescence", G. G. Guilbault, Ed., Arnold Ltd., London, 1967). The reported quantum yield of isc of P^{*1} is 0.76 [A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965)]; i.e. $(k_1 + k_2 + k_3) = 1.8 \times 10^7\ sec^{-1}$, and $k_3 = 1.37 \times 10^7\ sec^{-1}$.

(19) N. J. Turro, N. E. Shore, H.-C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **96**, 1936 (1974).

(20) Furthermore, in the present case, the quencher used (2,3-dimethylbutadiene) has a triplet energy only 2 kcal/mol lower than that of P and, if there is any interaction in the complex E^{*3} between P^{*3} and F, the difference in triplet energy between the quencher and the complex will be even smaller, which will result in a quenching rate below that of the *upper limit*. The *quenching* of a complex *might* also be slower than that of a molecular species owing to steric interaction.

(21) (a) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969); (b) C. Lewis and W. R. Ware, *Mol. Photochem.*, **5**, 261 (1973).

(22) M. P. Rappoldt, Dissertation, Leiden University (1958); cf. also G. O. Schenck in A. Schönberg, "*Preparative Organic Photochemistry*", Springer-Verlag, West Berlin, 1968, p 491.

(23) The AA′BB′ spectrum indicates that the two carbomethoxy groups have cis configuration. The negative value of the 1,3-coupling constant (^4J) is consistent with the anti (or exo) structure [R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965); C. H. Kranch, S. Farid, and G. O. Schenck, *ibid.*, **99**, 625 (1966); R. Mondelli and A. Gamba, *Org. Magn. Reson.*, **5**, 101 (1973)]. Caldwell[4] came to the same conclusion on the basis of ozonolysis experiments.

The SRN1 Mechanism in Heteroaromatic Nucleophilic Substitution. An Investigation of the Generality of Photostimulated Reactions of Ketone Enolates with 2-Chloroquinoline[1]

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Abstract: Secondary and tertiary lithium enolates, derived from a series of representative ketones, fail to react with 2-chloroquinoline (**1**) in liquid ammonia by the expected SRN1 mechanism when irradiated at 3500 Å. However, the corresponding potassium enolates react smoothly with **1** via this mechanism when subjected to photostimulation. With mixtures of primary and tertiary potassium enolates, quinolyl radicals, unlike phenyl radicals generated under similar conditions, show appreciable preference for combination with tertiary enolates. When **1** and iodobenzene are present in the same reaction mixture, potassioacetone reacts preferentially with the former under photostimulation. Potassio salts derived from β-dicarbonyl compounds do not undergo photostimulated SRN1 reaction with **1**, even when the potassium enolate of 2,4-dimethyl-3-pentanone is added to the reaction mixture as a potential entraining agent.

Recently, we presented evidence that the lithium salts of acetone and acetophenone react with 2-chloroquinoline (**1**) in liquid ammonia under near-ultraviolet irradiation to produce the appropriate α-(2-quinolyl) ketones via the radical-chain mechanism shown in Scheme I.[2] Photostimulation[3] apparently causes enhancement of the electron-transferring ability of the enolate ion, thereby permitting it to initiate the chain process by donating an electron to the heterocyclic substrate (step 1); steps 2–4 are propagating reactions. Similar reactions, designated by Bunnett[4] as SRN1, have been verified for reactions of carbanionic nucleophiles with aliphatic[5] and carboaromatic[4,6] systems containing appropriate nucleofugic groups. However, reports of related radical-chain pathways in heteroaromatic nucleophilic substitution are rare,[2,7] and photostimulation has not been generally recognized as a method for promoting such reactions.

Scheme I[a]

$$\mathrm{ClQ + RCOCH_2^- \longrightarrow ClQ\cdot^- + RCOCH_2\cdot} \tag{1}$$

$$\mathrm{ClQ\cdot^- \longrightarrow Q\cdot + Cl^-} \tag{2}$$

$$\mathrm{Q\cdot + RCOCH_2^- \longrightarrow QCH_2COR\cdot^-} \tag{3}$$

$$\mathrm{QCH_2COR\cdot^- + ClQ \longrightarrow QCH_2COR + ClQ\cdot^-} \tag{4}$$

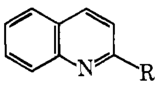
[a] ClQ = 2-chloroquinoline

We now describe the results of a study undertaken to test the generality of photostimulated SRN1 reactions of **1** with secondary and tertiary ketone enolates, as well as with enolates derived from β-dicarbonyl compounds.

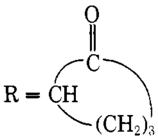
Results and Discussion

Metallic Cation Effects. Reaction of **1** with the secondary enolate, 2-lithio-3-pentanone, prepared from 4 mol equiv of lithium amide and 3 mol equiv of 3-pentanone in liquid ammonia, afforded none of the expected ketone **2**, following irradiation of the reaction mixture at 3500 Å for 1 hr. Instead, the isolated products were quinoline (12%), 2-aminoquinoline (21%), 2,3′-biquinoline (**8**) (13%), and unaltered **1** (45%). Analogous results were obtained in the presence of excess lithium amide, which has been shown[2] to facilitate the photostimulated reaction of lithioacetone with **1**. Similarly, the lithium enolates of propiophenone and 3-methyl-2-butanone failed to yield more than traces of the desired quinolyl ketones, even in the presence of excess lithium amide. The same series of side products was detected in each case.

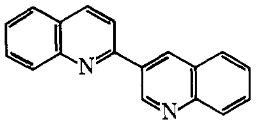
The results observed in the photostimulated reactions of secondary and tertiary lithium enolates with **1** are in sharp constrast to those obtained in comparable reactions of lithioacetone with **1**, where ketone **6** is produced in 62% yield after 1 hr by a photostimulated SRN1 process.[2] The formation of substantial amounts of quinoline in the present reactions involving secondary and tertiary lithium enolates offers evidence that steps 1 and 2 of the radical-chain mechanism shown in Scheme I do occur to some extent, but that the quinolyl radicals thus formed undergo competing reactions in preference to chain-carrying combination with the lithium enolates.[8] One such competing reaction could be the reduction of quinolyl radicals to quinolyl anions, which are then protonated by ammonia to form quinoline. The electron source in this case may be the lithium enolate, which reacts with quinolyl radicals as an electron-transfer agent rather than as a nucleophile.[5e] Formation of quinoline may also result from hydrogen atom transfer from the ether cosolvent to quinolyl radicals.[4] It is conceivable that 2-aminoquinoline and dimer **8** may also rise through initial formation of quinolyl radicals, although some of the former product could be produced by a conventional addition-elimination (SNAr) mechanism.[9]



1, R = Cl
2, R = $CH(CH_3)COCH_2CH_3$
3, R = $CH(CH_3)COC_6H_5$
4, R =



5, R = $C(CH_3)_2COCH(CH_3)_2$
6, R = CH_2COCH_3
7, R = $CH_2COC_6H_5$



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In reactions involving the lithium salts of 3-pentanone, propiophenone, and 3-methyl-2-butanone, we noted that these enolates were considerably less soluble in liquid ammonia than the lithium enolates of acetone and acetophenone, both of which reacted with **1** to form 2-quinolyl ketones, unaccompanied by significant amounts of by-products. This limited solubility appears to be important in determining the course of the present reactions since the competing processes encountered with secondary and tertiary lithium enolates were largely eliminated by utilization of the corresponding potassium salts, which are soluble in liquid ammonia. For example, reaction of 2-potassio-3-pentanone with **1** afforded, after 1 hr of photostimulation, 68% of ketone **2**, 2% of quinoline, and 14% of unreacted **1** (Table I). 2-Aminoquinoline and dimer **8** were not detected in the crude reaction product. The radical-chain character of this process was supported by the observation that only 4% of **2** was formed in a similar reaction conducted in the presence of 5 mol % of *p*-dinitrobenzene (DNB), a well-established inhibitor of SRN1 reactions.[5d,e]

Table I. Photostimulated Reactions of Potassium Enolates with 2-Chloroquinoline (**1**)[a]

Starting ketone	Product distribution[b] 2-Quinolyl ketone No.	2-Quinolyl ketone %	Quinoline, %	Recovered **1**, %
3-Pentanone	2	68 (38)	2	14
3-Pentanone[c,d]	2	4	3	76
Propiophenone	3	50 (31)	*f*	*f*
Cyclopentanone	4	63 (44)	*f*	*f*
2,4-Dimethyl-3-pentanone	5	94 (68)	5	0.0
2,4-Dimethyl-3-pentanone[e]	5	98	2	0.0
Acetone	6	90 (55)	4	0.0
Acetone[c]	6	2	3	91
Acetone[g]	6	1	2	86
Acetone[g–i]	6	43	29	*f*
Acetone[j]	6	65	3	20
Acetone[e]	6	66	3	32
Acetophenone	7	Trace	*f*	*f*
Acetophenone[k]	7	14	*f*	*f*
2,4-Dimethyl-3-pentanone and acetone	5 6	74 23	6	0.0
3-Methyl-2-butanone	11 12	13 62	5	6

[a] All reactions, unless otherwise noted, were carried out in 250 ml of anhydrous liquid ammonia under a nitrogen atmosphere and were irradiated with 3500 A light for 1 hr. [b] Yields were determined by VPC analysis; figures in parentheses represent isolated yields. No attempts were made to optimize isolated yields. [c] Reaction carried out in the presence of 5 mol % (based on **1**) of DNB. [d] 2-Aminoquinoline was formed in 14% yield. [e] Reaction time 15 min. [f] Not determined. [g] Reaction performed in the "dark". [h] Reaction promoted by 1 mol equiv (based on **1**) of potassium metal. [i] 2-Aminoquinoline was formed in 2.0% yield. [j] Reaction carried out in the presence of **1** mol equiv (based on **1**) of iodobenzene. [k] Reaction time, 3 hr.

Reactions of the potassium enolates of propiophenone, cyclopentanone, 2,4-dimethyl-3-pentanone, and acetone with **1** proceeded cleanly when subjected to irradiation for 1 hr at −33° to give 2-quinolyl ketones **3–6** in yields of 50–95% (Table I). In all cases, the ratio of enolate to **1** was 3.75:1, and excess potassium amide was not employed. Thus potassioacetone reacts smoothly with **1** in the absence of excess potassium amide whereas, under essentially identical conditions, displacement of chloride ion from **1** by lithioacetone requires excess lithium amide.[2] Although we still seek an explanation for this phenomenon, the enhanced reactivity of potassioacetone with **1** was shown not to result from a change in mechanism from SRN1 with lithioacetone to a rapid SNAr mechanism with the potassium salt. This conclusion was supported by the lack of reactivity of potassioacetone toward **1** in the absence of illumination and in the presence of catalytic amounts of DNB.

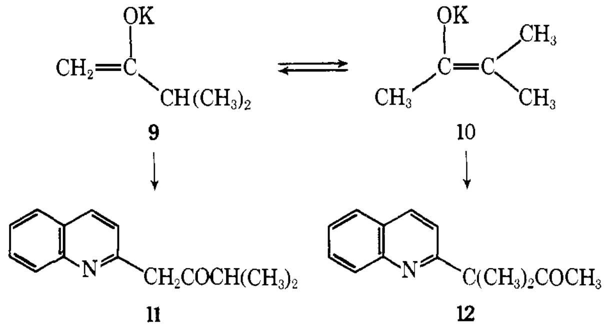
Among the enolates studied, the potassium salts of acetone and 2,4-dimethyl-3-pentanone appear to be the most effective initiators of the radical-chain process, as evidenced by the formation of ketones **5** and **6** in yields of 94 and 90%, respectively. One anomaly encountered in this series of experiments involved reaction of potassioacetophenone with **1**, which required prolonged (3 hr) irradiation to give only a modest (14%) yield of ketone **7**. These results differ from our earlier observation[2] that lithioacetophenone reacts rapidly with **1** under photostimulation to afford **7** (82%), and that the potassium enolate of propiophenone reacts satisfactorily with **1** (50% yield of ketone **3**) after 1 hr of illumination.

The SRN1 reaction of potassioacetone with **1** could also be promoted by potassium metal[4] without external illumination. Thus, addition of 1 mol equiv of potassium to a solution of potassioacetone and **1** in liquid ammonia effected a vigorous exothermic reaction. After 1 hr, the crude reaction product was found to contain ketone **6** (43%) and quinoline (29%). Compared with the photostimulated reaction, the increase in production of quinoline at the expense of **6** in the metal-promoted reaction can be attributed to reduction of quinolyl radicals to quinolyl anions by solvated electrons before the radicals can combine with enolate ions in a chain-propagating process. Previous attempts[2] to catalyze the reaction of lithioacetone with **1** by means of lithium metal gave ketone **6** in a maximum yield of 15%. Such lithium-promoted reactions also produced dimer **8** in yields of 13–18%, whereas only minor amounts of **8** were formed employing the potassium enolate–potassium metal combination.

Competitive Reactions. Having established that, except for potassioacetophenone, potassium enolates of simple aliphatic ketones react cleanly with **1** by an SRN1 mechanism upon photostimulation, we turned our attention to a study of several types of competitive reactions. In the first of these, equimolar amounts (37.5 mmol of each) of the potassium enolates of acetone and 2,4-dimethyl-3-pentanone, both of which had been shown to be highly efficient electron donors, were allowed to react with **1** (20 mmol). After 1 hr of irradiation, ketones **5** and **6** had been formed in yields of 74 and 23%, respectively. Although it has been suggested that the rate of combination of phenyl radicals with enolates is independent of the number of α substituents on the enolate,[6a] the results observed in this experiment clearly indicate that quinolyl radicals are fairly selective, with attack at the tertiary enolate site being favored over combination at the primary position by a 3:2:1 ratio. The greater reactivity of a tertiary enolate vs. a primary enolate with quinolyl radicals was also supported by separate short reactions of these two potassium salts with **1.** With 2,4-dimethyl-2-potassio-3-pentanone, ketone **5** was produced almost quantitatively after only 0.25 hr, while ketone **6** was formed from potassioacetone in 66% yield under identical conditions. In such individual experiments, both the nucleophilicity and electron-donating ability of the respective enolates can contribute to the observed rates of reaction. Thus, if the tertiary enolate were the more effective electron donor, it could be consumed more rapidly than the primary enolate, even though the relative nucleophilicities of both enolates toward quinolyl radicals were comparable. However, in competitive reactions involving equimolar amounts of primary and tertiary enolates, the rate of production of quinolyl radicals should not affect the distribution of ketonic products, which then becomes dependent only upon the relative rates of combination of quinolyl radicals with the respective carbanionic centers.

It should be noted that the absence of products resulting from attachment of more than one quinolyl group to the parent ketone residues is also consistent with the hypothesis that quinolyl radicals are less reactive (more selective) than phenyl radicals in SRN1 reactions with enolate ions. By comparison, the photostimulated reaction of potassioacetone with iodobenzene produces 10% of 1,1-diphenyl-2-propanone.[3]

The next series of competitive experiments was designed to test the reactivity of quinolyl radicals toward a mixture of enolates derived from a single ketone substrate. 3-Methyl-2-butanone, which can form isomeric enolates **9** and **10,** was treated with potassium amide and then **1**. After 1 hr of illumination, the crude reaction product was found to contain 62% of ketone **11,** 13% of **12,** 5% of quinoline, and 6% of unchanged **1.** This product ratio (4.75:1) of **11:12** differs significantly from the reported 9:1 ratio of the analogous phenyl ketones produced by phenylation of enolates **9** and **10** under similar conditions.[6a] It has been proposed[6a] that the ratio of ketones resulting from photostimulated SRN1 phenylation of **9** and **10** reflects the equilibrium composition of the potassium enolate mixture in liquid ammonia. This suggestion has been supported recently by studies in which an equilibrium mixture of potassio salts **9** and **10** in THF was reported to contain ca. 98% of **9.**[10]



In the present case, the high selectivity of quinolyl radicals for the tertiary enolate presumably results in more rapid consumption of **10** than **9,** thereby allowing equilibrium to be in effect shifted toward the more highly substituted enolate. As a result of this selectivity, a higher proportion of ketone **12** is observed than in the analogous process involving combinations of the more reactive, but less selective, phenyl radical with enolates **9** and **10.**

Finally, in order to determine if any differences could be observed in the SRN1 reactivity of halogenated heteroaromatic vs. halogenated carboaromatic substrates, we carried out the photostimulated reaction of potassioacetone with **1** in the presence of a mol equiv (based on **1**) of iodobenzene. After 1 hr of irradiation, ketone **6** had been produced in 65% yield, along with 3% of quinoline and 20% of unreacted **1.** Only a trace (<1%) of phenylacetone was detected. Employing similar conditions, Rossi and Bunnett[3] have found that iodobenzene is completely consumed by potassioacetone after 5 min in the absence of **1.**

The selectivity of acetone enolate toward **1** is attributed to the relative ease of reduction of the individual substrates to the corresponding radical anions in the initiation step, with **1** being able to accept an electron more readily than iodobenzene.[11] It is interesting that the presence of **1** in the reaction mixture containing iodobenzene almost totally inhibits the phenylation of potassioacetone. In addition, the yield of ketone **6** is somewhat lower than that observed in the absence of iodobenzene. It is possible that quinolyl radicals serve not only to combine with the enolate ion but also to inhibit chain-carrying reactions involving phenyl radicals.

β-Dicarbonyl Enolates. In this series of experiments, potassium enolates of several β-dicarbonyl compounds were employed to determine if they would react with **1** in a radical-chain manner. Treatment of the potassium salt of 2,4-pentanedione with **1** afforded, after 1 hr of photostimulation, predominantly unreacted **1** and 2,4-pentanedione. Similarly, the potassio salts of ethyl acetoacetate and diethyl malonate afforded only unaltered starting reagents after 1 hr of illumination.

There appear to be three possible reasons for the failure of β-dicarbonyl enolates to react with **1** in a radical-chain manner: (1) the enolates do not possess sufficient electron-donating character to initiate the SRN1 process; (2) the nucleophilicities of the enolates are not great enough to allow combination with quinolyl radicals; and/or (3) quinolyl radicals and the enolates combine, but the product radical anion (Scheme I, step 3) is unable to transfer an electron to **1**, thereby causing interruption of the chain sequence. The first of these three factors can in principle be tested by use of an entraining agent.[12] Such a reagent, possessing sufficiently powerful electron-donating capacity toward **1** to initiate the radical-chain process, could enable the SRN1 reaction to proceed with an anion whose reducing power is too weak to start the chain reaction. The potassium enolate of 2,4-dimethyl-3-pentanone, which had been found to be a highly efficient initiator of the radical-chain reaction with **1**, was used as a potential entraining agent in the photostimulated reaction of diethyl potassiomalonate with **1**. After 1 hr of irradiation, only unreacted **1**, diethyl malonate, and a small amount of ketone **5**, formed via combination of quinolyl radicals with the entraining agent, were obtained. This experiment indicates that the failure of malonate anion to participate in a SRN1 reaction with **1** must be due to either the low nucleophilicity of the enolate or the occurrence of chain-terminating reactions between the enolate and quinolyl radicals. Since other investigators[13] have found that β-dicarbonyl enolates combine readily with radicals such as *p*-nitrobenzyl, we currently favor the latter explanation. Work aimed at further elucidating the mechanistic details of reactions involving heterocyclic radicals and stabilized enolates is continuing.

Summary

On the basis of the present results, several generalizations concerning heteroaromatic SRN1 processes have begun to emerge. First of all, in photostimulated reactions involving simple ketone monoenolates, potassio salts are generally preferable to the less soluble lithium enolates, with photostimulation being more effective than catalysis by solvated electrons. Secondly, quinolyl radicals show a higher degree of selectivity toward isomeric enolates than do phenyl radicals. Thirdly, heteroaromatic SRN1 substitution is favored over carboaromatic SRN1 displacement, at least with 2-chloroquinoline vs. iodobenzene. Finally, β-dicarbonyl enolates appear to be reluctant participants in heteroaromatic SRN1 substitution, even under conditions of photostimulation or entrainment.

Experimental Section

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. Proton magnetic resonance ^{1}H NMR spectra were recorded on a JEOL JMN-PS-100 instrument, employing tetramethylsilane as internal standard. Infrared (ir) spectra were obtained on a Beckman IR 20A-X spectrophotometer. Microanalyses were performed in this laboratory by T. E. Glass employing a Perkin-Elmer 240 elemental analyzer. Analytical vapor phase chromatography (VPC) was carried out on a Varian Aerograph Model 90-P chromatograph. Reactions involving the enolates of acetone, 3-pentanone, 3-methyl-2-butanone, and 2,4-dimethyl-3-pentanone were analyzed at 235° on a column of 6.3% Carbowax 20M on Gas Chrom Z, employing 4-methylquinoline as internal standard. Reactions involving all other enolates were analyzed at 250° on a column of 4% silicone rubber SE-30 on Chromosorb W, employing benzyl benzoate as internal standard. Thin layer chromatography (TLC) analyses were performed on Eastman chromagram (Type 6060) silica gel sheets with fluorescent indicator, employing ether–hexane (6:4) as developing solvent; components were detected with uv light. Photostimulated reactions were conducted in a Rayonet RPR-208 photochemical reactor equipped with four 24-W 3500 Å lamps.

Authentic samples of several ketones obtained in photostimulated SRN1 reactions were synthesized by more traditional methods for use as VPC standards.

1-(2-Quinolyl)-3-methyl-2-butanone (**11**) was prepared in 53% yield by the procedure of Wiess and Hauser:[14] bp 126–128° (1 mm) [lit.[14] bp 144° (2.5 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 6 H, CH_3), 2.57 (septet, 1 H, CH), 4.16 (s, 0.2 H, CH_2), 5.36 (s, 0.8 H, vinyl), 6.61 (d, 1 H, aromatic), and 7.08–7.88 ppm (m, 5 H, aromatic).

3-Methyl-3-(2-quinolyl)-2-butanone (**12**) was prepared in 49% yield by dimethylation of 2-acetonylquinoline (**6**), employing sodium hydride as the ionizing base and methyl iodide as the alkylating agent, bp 116–118° (1.1 mm). Preparative VPC afforded analytically pure material: ir ($CHCl_3$) ν 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.62 (2, 6 H, CH_3), 2.04 (s, 3 H, CH_3), 7.36–7.91 (m, 4 H, aromatic), and 8.20 ppm (d, 2 H, aromatic).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.58; H, 7.37; N, 6.67.

2-Phenacylquinoline (**7**) was prepared by the method of Wiess and Hauser[14] in 61% yield: mp 114.5–118° (lit.[14] mp 114–116°); ^{1}H NMR ($CDCl_3$) δ 4.27 (s, 0.75 H, CH_2), 6.04 (s, 0.64 H, vinyl), and 7.17–8.25 ppm (m, 11 H, aromatic).

Photostimulated Reaction of 2-Chloroquinoline (1) with the Lithium Enolate of 3-Pentanone. The reaction was performed in a 500-ml three-necked flask equipped with a mechanical stirrer, and a solid CO_2–2-propanol condenser fitted with a nitrogen inlet. Lithium metal (0.14 g, 20 mg-atoms) was added to 250 ml of anhydrous liquid ammonia in the reaction flask, and a crystal of ferric nitrate was added to catalyze the formation of lithium amide. 3-Pentanone (1.29 g, 15 mmol) in 20 ml of anhydrous ether was added slowly, and the resulting tan suspension was stirred for 10–15 min to assure formation of the enolate. Irradiation of the reaction mixture was begun, and **1** (0.82 g, 5 mmol) in 40 ml of anhydrous ether was added. After 1 hr, the reaction was quenched with excess solid ammonium chloride. The ammonia was evaporated (hot air gun), while being replaced with an equal volume of ether. Water (100 ml) was added, and the organic phase was separated. The aqueous phase was extracted with two 50-ml portions of ether; the combined organic solution was dried ($MgSO_4$) and concentrated. The resulting brown oily solid was chromatographed on silica gel; elution with hexane–ether (95:5) gave 0.37 g (45% recovery) of unreacted **1** followed by 0.08 g (12%) of quinoline. Elution with hexane–ether (85:15) afforded 0.08 g (12%) of 2,3′-biquinoline (**8**), mp 175–177.5°, after recrystallization from acetone–hexane (lit.[15] mp 175°): mass spectrum (*m/e*) 256 (M^+) (calcd for $C_{18}H_{12}N_2$, 256); ^{1}H NMR ($CDCl_3$) δ 7.44–8.08 (m, 7 H), 8.88 (d, 1 H, J = 2.0 Hz), and 9.80 ppm (d, 1 H, J = 2.0 Hz).[16] Elution with hexane–ether (1:1) afforded 0.15 g (21%) of 2-aminoquinoline, mp 128–129° (lit.[17] mp 129°): ^{1}H NMR (DMSO-d_6) δ 6.40 (s, 2 H, NH_2), 6.72 (d, 1 H, J = 8.0 Hz), 7.09 (m, 1 H), 7.41 (m, 2 H), 7.59 (d, 1 H), and 7.81 ppm (d, 1 H, J = 8.0 Hz).

A similar product distribution was observed in the photostimulated reaction of **1** with the lithium enolates of propiophenone and 3-methyl-2-butanone.

Photostimulated Reactions of Potassium Enolates with 1. The photostimulated reaction of **1** with the potassium enolate of 3-pentanone is representative and is described in detail. In all cases where isolated product yields are presented, identical experiments were carried out to obtain the VPC yields given in Table I.

A. 2-(2-Quinolyl)-3-pentanone (2). A solution of 3-pentanone (6.45 g, 75 mmol) in 25 ml of ether was added slowly to a solution of potassium amide (75 mmol), prepared from 2.93 g (75 mg-atoms) of potassium metal, in 250 ml of liquid ammonia under a nitrogen atmosphere. The enolate was allowed 10–15 min to form, irradiation was begun, and **1** (3.27 g, 20 mmol) in 50 ml of ether was added. After 1 hr, the reaction was quenched with excess ammonium chloride and then processed as in the previous experiment. The crude product was distilled to afford 1.64 g (38%) of 2-(2-quinolyl)-3-pentanone (**2**): bp 131–132° (1.3 mm); ir ($CHCl_3$) ν 1714 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.01 (t, 3 H, CH_3), 1.61 (d, 3 H, CH_3), 2.55 (q, 2 H, CH_2), 4.27 (q, 1 H, CH), 7.32–7.89 (m, 5 H, aromatic) and 8.16 ppm (d, 1 H, aromatic).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84, H, 7.09, N, 6.57. Found: C, 78.89; H, 7.04; N, 6.62.

B. 1-Phenyl-2-(2-quinolyl)-1-propanone (3). The photostimulated reaction of **1** with the potassium enolate of propiophenone gave **3** (32%): bp 176–180 (1.1 mm); mp 92–98°. Recrystallization from pentane gave analytically pure material: mp 100–101.5°; ir ($CHCl_3$) ν 1710 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$) δ 1.68 (d, 3 H,

CH_3), 5.17 (q, 1 H, CH), 7.22–7.79 (m, 8 H, aromatic), and 7.99–8.18 ppm (m, 3 H, aromatic).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.75; H, 5.78, N, 5.36. Found: C, 82.48; H, 5.91; N, 5.65.

C. 2-(2-Quinolyl)cyclopentanone (4). Distillation of the crude product obtained from the photostimulated reaction of **1** with the potassium enolate of cyclopentanone afforded **4** (44%): bp 163–167° (1.1 mm); mp 93–100° (lit.[18] mp 99–101°); ^1H NMR ($CDCl_3$) δ 1.96 (m, 2 H, CH_2), 5.44 (s, 0.25 H, CH), 6.68 (d, 1 H, aromatic), and 7.12–7.92 ppm (m, 5.7 H, aromatic). Ketone **4** was found to be rather unstable, undergoing appreciable decomposition and darkening after 24 hr at 25° in a closed vial.

D. 2,4-Dimethyl-2-(2-quinolyl)-3-pentanone (5). The photostimulated reaction of **1** with the potassium enolate of 2,4-dimethyl-3-pentanone gave **5** (68%): bp 131–132° (1.3 mm); ir ($CHCl_3$) ν 1708 cm^{-1} (C=O); ^1H NMR δ 0.95 (d, 6 H, $CH(CH_3)_2$); 1.67 (s, 6 H, CH_3), 2.77 (septet, 1 H, CH), 7.44 (d, 1 H, aromatic), 7.52–7.89 (m, 4 H, aromatic), and 8.18 ppm (d, 1 H, aromatic).

Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.81. Found: C, 79.81; H, 7.76; N, 5.87.

When a similar reaction was quenched after 15 min of irradiation, VPC analysis indicated a quantitative yield of ketone **5**.

E. 2-Acetonylquinoline (6). Photostimulation of the reaction of **1** with potassioacetone gave, by trituration of the crude product with pentane, **6** (55%): mp 71–74° (lit.[14] 76–77°); ^1H NMR (DMSO-d_6) δ 2.08 (s, 2 H, CH_3, enol), 2.28 (s, 1 H, CH_3, keto), 4.18 (s, 0.7 H, CH_2), 5.40 (s, 0.6 H, vinyl), and 6.84–8.26 ppm (m, 6 H, aromatic).

VPC analysis of a similar reaction quenched after 15 min showed that ketone **6** had been produced in 66% yield.

F. 1-(2-Quinolyl)-3-methyl-2-butanone (11) and 3-Methyl-3-(2-quinolyl)-2-butanone (12). VPC analysis of the photostimulated reaction of **1** and the potassium enolate mixture derived from 3-methyl-2-butanone indicated a 62% yield of **12**, 13% of **11**, 5% of quinoline, and 6% of unreacted **1**.

G. 2-Phenacylquinoline (7). VPC analysis of the photostimulated reaction of **1** with the potassium enolate of acetophenone showed only a trace of **7** after 1 hr of photolysis. Extended photostimulation (3 hr) of this enolate with **1** afforded a 14% yield (VPC) of **7**.

Photostimulated Reactions of 1 with Potassium Enolates in the Presence of *p*-Dinitrobenzene (DNB). The reaction employing 2-potassio-3-pentanone is representative.

A solution of the potassium enolate of 3-pentanone (75 mmol) in 250 ml of liquid ammonia was prepared as previously described. DNB (1 mmol) was added as a solid, irradiation of the resulting purple solution was begun, and a solution of **1** (20 mmol) in 50 ml of ether was added. After 1 hr, the reaction was quenched with excess ammonium chloride, processed in the usual manner, and analyzed by VPC.[19]

Reaction of 1 with Potassioacetone in the "Dark". The reaction was performed as other liquid ammonia reactions of potassium enolates with **1**, except that the reaction flask was enclosed in aluminum foil and was not irradiated. VPC analysis of the crude product mixture was carried out after 1 hr.

Potassium Metal-Promoted Reaction of Potassioacetone with 1. A solution of potassioacetone (75 mmol) in 250 ml of liquid ammonia was prepared as before. A solution of **1** (20 mmol) in 50 ml of ether was added, followed immediately by potassium metal (20 mmol). A vigorous exothermic reaction ensued with the formation of a deep red-brown color. After 1 hr, the reaction was quenched with excess solid ammonium chloride, processed in the usual manner, and analyzed by VPC.

Competitive Photostimulated Reactions of 1 with the Potassium Enolates of Acetone and 2,4-Dimethyl-3-pentanone. A solution of acetone (37.5 mmol) and 2,4-dimethyl-3-pentanone (37.5 mmol) in 25 ml of ether was added to a solution of potassium amide (75 mmol) in 250 ml of liquid ammonia under a nitrogen atmosphere. After 15 min, irradiation was begun, and **1** (20 mmol) in 50 ml of ether was added. The reaction was quenched after 1 hr with excess solid ammonium chloride and then processed and analyzed by VPC in the usual fashion.

Photostimulated Reaction of 1 with Potassioacetone in the Presence of Iodobenzene. Irradiation of a solution of potassioacetone (75 mmol) in 250 ml of liquid ammonia was begun, and a solution of **1** (20 mmol) and iodobenzene (20 mmol) in 50 ml of ether was added. After 1 hr, the reaction was quenched with excess solid ammonium chloride, processed in the normal manner, and subjected to VPC analysis. Only a trace of phenylacetone was detected.

References and Notes

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