Photostimulated Arylation of Ketone Enolate Ions by the SRN1 Mechanism[1,2,3]

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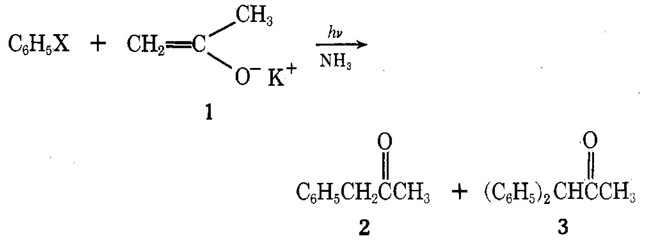
Enolate ions from several open-chain and cyclic ketones react with bromo- or iodobenzene in liquid ammonia, under irradiation, to form α-phenyl derivatives of the ketones. The reaction is of wide scope, but it fails with the enolate ions of acetophenone and of several β-dicarbonyl compounds, and is impeded by appreciable steric hindrance. The lethargic reaction of iodobenzene with the enolate ion of diisopropyl ketone afforded, besides some α-phenyl ketone, nearly equal yields of benzene and of a hexamethyloctanedione; this provides insight into a yield-limiting and rate-depressing side reaction. The dianion of 2,4-pentanedione is mesitylated by 2-bromomesitylene at the terminal carbon in high yield.

In 1972 it was discovered[4] that acetone enolate ion (**1**) reacts readily with unsubstituted phenyl halides in liquid ammonia under photostimulation to form phenylacetone (**2**), accompanied by some 1,1-diphenyl-2-propanone (**3**).



Later it was shown that enolate ions derived from 2-butanone and 3-methyl-2-butanone are similarly phenylated,[5] that acetone enolate ion can be arylated by a great variety of aryl halides,[6] that ketone enolate ions can be 2-quinolinylated by photostimulated reaction with 2-chloroquinoline,[7] and that 1-chloronaphthalene reacts in similar fashion with the enolate ions of acetone and other ketones to form α-(1-naphthyl) derivatives of them.[8]

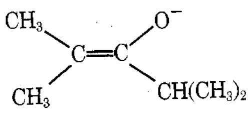
We now report a further study to establish the scope of this synthetic method. We have investigated reactions of bromo- or iodobenzene with enolate ions from diverse ketones, and in a few cases reactions of bromo- or iodomesitylene. The results illuminate aspects of the reaction mechanism, apart from their interest for synthesis.

Results

Reactions were conducted in liquid ammonia at reflux with irradiation through Pyrex from fluorescent lamps emitting maximally at 350 nm. Solutions of ketone enolate ions were prepared by reaction of the ketone with a slight excess of potassium *tert*-butoxide (*t*-BuOK) in ammonia. Except in a few special cases, the ketone enolate ion was in approximately a threefold excess over the aryl halide during irradiation.

The ten experiments summarized in Table I concern reactions with the enolate ions of noncyclic ketones. 3-Pentanone (expt 4) and 4-heptanone (expt 7) are phenylated at α positions in 80% yield, and the yield is even higher for phenylation of 3,3-dimethyl-2-butanone at the 1 position (expt 3). In these cases, the chief interference is by a second stage of phenylation to form diphenyl derivatives of the starting ketones.

2,4-Dimethyl-3-pentanone (expt 5 and 6) furnishes a single enolate ion (**4**) in which the nucleophilic α carbon carries two methyl substituents. The photostimulated phenylation of it is sluggish. Under conditions conducive to complete reaction with other enolate ions, reaction of either bromo- or iodobenzene with **4** was incomplete. Recoveries of unreacted halobenzene were 85 and 48%, respectively. Modest yields of the expected α-phenylation product were obtained in both cases. The most interesting product, however, was 2,4,4,5,5,7-hexamethyloctane-3,6-dione (**5**), which can be considered an oxidative dimer of **4**. In expt 6, this was accompanied by a nearly equal yield of benzene, a product of reductive deiodination.



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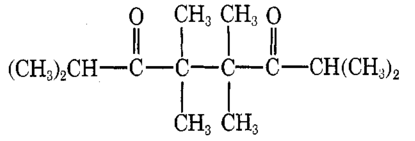


$$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$$

5

In contrast to these observations, Wolfe and Hay[9] found that the photostimulated reaction of enolate ion **4** with 2-chloroquinoline occurs readily to form an α-arylation product in high yield.

The mesitylation by either bromo- or iodomesitylene of the enolate ions derived from 3-pentanone (expt 9 and 10) is also sluggish. In both cases half or more of the mesityl halide was recovered after reaction times ample for their complete consumption in reaction with acetone enolate ion[6] or for complete reaction of bromobenzene with the enolate ions of 3-pentanone (expt 4). Appreciable amounts of mesitylene were formed in both expt 9 and 10. This suggests a complication analogous to that encountered in expt 5 and 6, but in this case no ketone dimer was obtained as a product.

Phenylation of the enolate ions of methoxyacetone was also lethargic; see expt 8. After 130 min of irradiation, less than 1% of a product that is possibly 1-phenyl-1-methoxy-2-propanone was formed, and 78% of the bromobenzene was recovered. The principal product was phenylacetone, which presumably represents loss of a methoxy group after attachment of phenyl.

Remarkably, the enolate ion of acetophenone is totally unreactive with bromo- or iodobenzene (expt 1 and 2). Even when 10% of acetone enolate ion was also present (an experiment not tabulated), bromobenzene failed to phenylate acetophenone enolate ion. The photostimulated α-naphthylation of acetophenone enolate ion by 1-chloronaphthalene is reported to occur, but very slowly, giving only 8% of α-(1-naphthyl)acetophenone after 3-h irradiation.[8] In contrast, 2-chloroquinoline reacts readily with acetophenone enolate ion under photostimulation to form 2-phenacylquinoline in 82% yield.[7]

Reaction of acetone enolate ion with a threefold excess of bromobenzene (experiment not tabulated) afforded, besides

Table I. Photostimulated Reactions of Phenyl and Mesityl Halides with Enolate Ions of Noncyclic Ketones in Liquid Ammonia

Expt no.	Aryl halide[a]	Ketone	Registry no.	Irradiation time, min	Products[b]
1	PhBr	$PhCOCH_3$	98-86-2	140	PhBr, 99% Br^-, nil
2	PhI	$PhCOCH_3$		180	PhI, 99% I^-, nil
3	PhBr	$CH_3COC(CH_3)_3$	75-97-8	90	$PhCH_2COC(CH_3)_3$, 90% $Ph_2CHCOC(CH_3)_3$, 10% C_6H_6, trace
4	PhBr[c]	$CH_3CH_2COCH_2CH_3$[c]	96-22-0	70	$PhCH(CH_3)COCH_2CH_3$, 80% Diphenyl ketones,[d] 19% C_6H_6, trace
5	PhBr	$(CH_3)_2CHCOCH(CH_3)_2$	565-80-0	90	$PhC(CH_3)_2COCH(CH_3)_2$, 6% C_6H_6, 8% PhBr, 85% Ketone dimer[e,f]
6	PhI	$(CH_3)_2CHCOCH(CH_3)_2$		180	$PhC(CH_3)_2COCH(CH_3)_2$, 32% C_6H_6, 19% PhI, 48% Ketone dimer,[e] 20%[g]
7	PhBr	4-Heptanone	123-19-3	120	$PhCH(C_2H_5)COCH_2CH_2CH_3$, 80% Diphenyl ketones,[h] 10% C_6H_6, 11%
8	PhBr	$CH_3OCH_2COCH_3$	5878-19-3	130	$PhCH(OCH_3)COCH_3$, 0.9% $PhCH_2COCH_3$, 17% PhBr, 78% Br^-, 19%
9	MesBr	$CH_3CH_2COCH_2CH_3$		130	$MesCH(CH_3)COCH_2CH_3$, 14% s-$C_6H_3(CH_3)_3$, 20% MesBr, 58%
10	MesI	$CH_3CH_2COCH_2CH_3$		130	$MesCH(CH_3)COCH_2CH_3$, 24% s-$C_6H_3(CH_3)_3$, 25% MesI, 50%

[a] MesBr is mesityl bromide, etc. [b] Yields by isolation and weighing unless otherwise noted; halide ion yields by titration with $AgNO_3$. [c] Initial concentrations: PhBr, 0.043 M; enolate ions, 0.15 M. [d] Mixture of diphenyl-3-pentanone isomers. [e] 2,4,4,5,5,7-Hexamethyl-3,6-octanedione. [f] Yield not determined. [g] Yield by GLC. [h] Mixture of diphenyl-4-heptanone isomers.

Table II. Photostimulated Reactions of Bromobenzene with Enolate Ions of Cyclic Ketones in Liquid Ammonia

				Yields,[a] %				
Expt no.	Ketone	Registry no.	Irradiation time, min	PhBr	C_6H_6	α-Phenyl ketone	Br^-	Note
11	Cyclobutanone	1191-95-3	150	Tr	4	90	96	
12	Cyclopentanone	120-92-3	150	9	28	64	91	b
13	Cyclohexanone	108-94-1	60	18	6	72		
14	Cycloheptanone	502-42-1	210	29	12	58	70	
15	Cyclooctanone	502-49-8	210	0	3	95[c]	100	
16	2-Indanone	615-13-4	150	2	2	90	95	d
17	Cyclohex-2-en-1-one	930-68-7	100	92	3	0	8	

[a] Yields by GLC unless otherwise indicated. [b] Bicyclopentyl-2,2′-dione also formed; structure assigned from mass and infrared spectra. [c] Yield 92% by isolation and weighing. [d] Ca. 5% of 2,2′-biindanyl-1,1′-dione also formed; structure assigned from mass spectrum.

32% of phenylacetone (**2**), a 58% yield of 1,1-diphenyl-2-propanone (**3**). None of the symmetrical diphenyl derivative could be detected. Only a trace of a triphenylacetone, of undetermined structure, was found.

Enolate Ions from Cyclic Ketones. The enolate ions of the series cyclobutanone through cyclooctanone were irradiated in the presence of bromobenzene, the enolate ion always being in threefold excess. Results are displayed in Table II, expt 11–15.

A curious pattern emerges, in that the enolate ions of the "even" ketones, cyclobutanone, cyclohexanone, and cyclooctanone, react quite well to form α-phenyl derivatives in high yield, whilst phenylation of the "odd" enolate ions, those from cyclopentanone and cycloheptanone, is less satisfactory. The two "odd" ketones differ, however, in their behavior. The reaction with cyclopentanone enolate ion (expt 12) went nearly to completion but formed a rather large amount (28%) of benzene as well as another by-product which appears to be a ketone dimer, analogous to **5**. The reaction with cycloheptanone enolate ion (expt 14) left 29% of bromobenzene unreacted even after a long irradiation time. Dehalogenation to benzene (12%) was more prominent than with the "even" enolate ions but less than with cyclopentanone enolate ion.

2-Indanone enolate ion (expt 16) was phenylated in high yield. This is similar to the second stage of phenylation of acetone enolate ion, which goes rather well.

The enolate ions of the α,β-unsaturated ketone, cyclohex-2-en-1-one (expt 17), reacted very slowly with bromobenzene. No phenylation product could be found.

Enolate Ions from β-Dicarbonyl Compounds. In experiments not tabulated, but similar in design to those of Tables I and II, efforts were made to phenylate with bromobenzene the monoenolate ions of 2,4-pentanedione, 5,5-dimethyl-1,3-cyclohexanedione, and 1,3-indandione, and with iodobenzene those of diethyl malonate,[10] ethyl acetoacetate,[10] and 2,4-pentanedione. These efforts were all unsuccessful; no phenylation product was obtained (although there was mass spectral evidence of a trace of 3-phenyl-2,4-pentanedione from the iodobenzene reaction), and halide ion release was 12% or less.

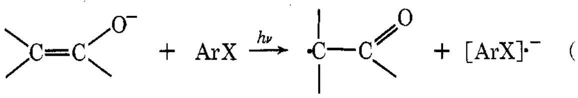
The dianion formed by treatment of 2,4-pentanedione with 2 equiv of KNH_2 was shown by Hauser and co-workers[11] to have high nucleophilic reactivity at the 1 carbon, much greater than at the 3 carbon. Also, the dianion of benzoylacetone was shown to react with 2-chloroquinoline in liquid ammonia preferentially by arylation at the terminal carbon.[12] The SRN1 mechanism was assigned to the latter reaction.

In seeking to determine whether the dianion of 2,4-pentanedione can be arylated by the SRN1 mechanism, we chose 2-bromomesitylene as arylating agent in order to avoid ambiguity as to whether a benzyne mechanism might be involved.[13] The phenylation of this dianion by the benzyne mechanism has been described, but the yield was poor.[11]

In our experiment (not tabulated), the photostimulated reaction of the dipotassium salt of 2,4-pentanedione with 2-bromomesitylene afforded 1-mesityl-2,4-pentanedione in 82% yield, together with 13% of mesitylene. Thus SRN1 arylation at the 1 carbon is very satisfactory.

Discussion

The arylation reactions we have observed are believed to occur by the SRN1 mechanism.[4,14] This mechanism, in schematic form suitable to the present case, is as follows.


(1)

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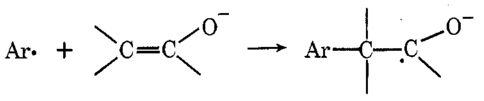
$$[ArX]\cdot^- \longrightarrow Ar\cdot + X^- \qquad (2)$$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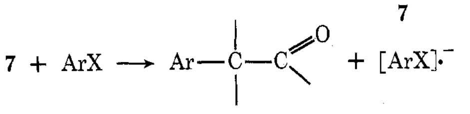

(4)

This is a radical chain mechanism of a type first proposed by Kornblum[15] and Russell[16] and their co-workers for certain substitutions at aliphatic sites. It was recognized as a mechanism of aromatic substitution in 1970.[14]

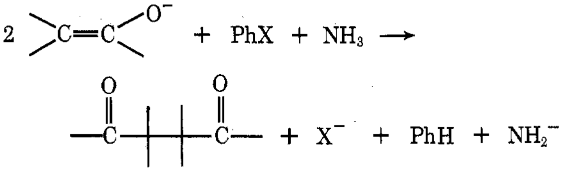
Initiation is represented to occur (step 1) by photostimulated transfer of an electron from the enolate ion to the aryl halide, forming the radical anion of the latter and a β-keto alkyl radical (6). Details of the electron transfer are unclear. A conceivable alternative, photolysis of the C–X bond of the aryl halide,[17] generating an aryl radical which enters the propagation cycle at step 3, is disfavored because iodo- and bromobenzene differ so little in their reactivity with ketone enolate ions.

The $[ArX]\cdot^-$ radical anion ejects halide ion in step 2, and the resulting aryl radical adds, in step 3, to the enolate ion to form species 7, which may be described as a radical anion or a ketyl. It may transfer an electron to another substrate molecule, in step 4, to form an α-aryl ketone and regenerate radical anion $[ArX]\cdot^-$. Steps 2, 3, and 4 constitute the propagation cycle of a chain mechanism. There must also be termination steps, of which we shall have more to say later.

Dehalogenation and Ketone Dimer Formation. Aromatic SRN1 reactions are remarkably insensitive to steric hindrance.[6,13] An example is our observation that the dianion of 2,4-pentanedione is mesitylated by 2-bromomesitylene in 82% yield. However, as the steric requirements of aromatic substituents or of enolate ions increase, both reactivity and yields of arylation products diminish. Thus, in expt 9 and 10, Table I, the mesitylation of 3-pentanone enolate ions is lethargic and the yields of 2-mesityl-3-pentanone produced are rather low. It is to be noted that they are accompanied by larger amounts of mesitylene, a dehalogenation product.

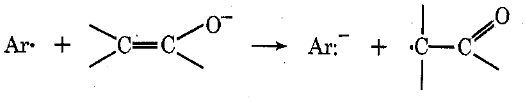
Indeed, inspection of our present results and of others published elsewhere[6] reveals a general tendency for the formation of dehalogenation products to be associated with low overall reactivity. See, for example, expt 5, 6, 12, and 14.

Insight is provided by our discovery of ketone dimer **5** as a by-product of the phenylation of 2,4-dimethyl-3-pentanone enolate ion (**4**) in expt 5 and 6. Significantly, the yield of benzene in expt 6 is equal to that of **5**, consistent with balanced eq 5.


(5)

8

Two mechanisms for the formation of **5** are conceivable. Both involve a second mode of interaction of aryl radical with enolate ion, as in step 6, which parallels step 3. This is an electron transfer, and the aryl anion that it forms rapidly takes a proton from the solvent (step 7). The other product of step 6 is β-keto alkyl radical **6**, the same as formed in step 1.


(6)

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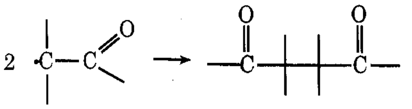
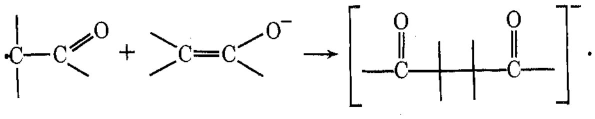
$$Ar\!:^- + NH_3 \longrightarrow ArH + NH_2^- \qquad (7)$$

One mode of reaction of β-keto radical **6** is dimerization to ketone dimer **8**, as in step 8. The sum of steps 1, 2, 6, 7, and 8 is eq 5, for which there is experimental support.


(8)

6 8

An alternative possibility is combination of radical **6** with enolate ion, and subsequent electron transfer to a substrate molecule, as in steps 9 and 10. For this alternative, the sum of steps 2, 6, 7, 9, and 10 amounts to eq 5.


(9)

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$$9 + ArX \longrightarrow [ArX]\cdot^- + 8 \qquad (10)$$

Thus the two alternatives both imply the same stoichiometry. Both are crucially dependent on step 6, for if the aryl radical and enolate ion simply combine as in step 3, radical **6** is not generated except in relatively small amounts in initiation step 1.

The alternatives differ, however, in one important respect. Step 8 in the set of steps 1, 2, 6, 7, and 8 is a termination step, whereas none of the set of steps 2, 6, 7, 9, and 10 is a termination step. Inasmuch as the formation of dehalogenation products, as well as ketone dimers as in expt 5, 6, 12, and 16, is associated with low overall reactivity, the alternative of steps 1, 2, 6, 7, and 8 is favored.

Dimerization of β-keto alkyl radicals (step 8) is precedented. In point of fact, we synthesized an authentic sample of diketone **5** by just such a reaction.[18]

One would anticipate from the literature that combination of a β-keto alkyl radical with an enolate ion, as in step 9, might well occur. Kornblum, Boyd, and Stuchal[19] present evidence that β-keto alkyl radicals combine in the suggested manner with nitronate ions. Moreover, the cathodic cleavage of 1,4-diketones to form enolate ions, which may involve the reverse of step 9, has been described.[20] Therefore the alternative of steps 2, 6, 7, 9, and 10, although disfavored, cannot be ruled out altogether.

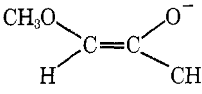
Presuming that we assess the situation correctly, we proceed to ask what determines whether an aryl radical interacts with an enolate ion by covalent bond formation (step 3) or electron transfer (step 6). Steric hindrance has something to do with it, for the formation of dehalogenation products and to some extent of ketone dimers is greater when the aryl radical and/or the enolate ion are cluttered with alkyl substituents. (In some of our experiments ketone dimers, which were not sought as products, may have escaped detection.) However, it is difficult to visualize much steric hindrance in the interaction of phenyl radical with the enolate ion of cyclopentanone (cf. expt 12) or even with **4** (cf. expt 5 and 6). Furthermore, why does the 2-quinolyl radical arylate **4** more rapidly than **1**, seemingly eschewing the electron transfer mode of reaction with **4**?[9] There is much yet to be learned.

Anions from β-Dicarbonyl Compounds. From time to time efforts have been made at Santa Cruz to involve the monoanions of β-dicarbonyl compounds as nucleophiles in aromatic $S_{RN}1$ reactions.[21] The results have been uniformly unrewarding.

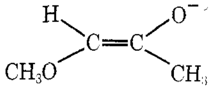
The failure of, for example, the diethyl malonate anion to be arylated by bromobenzene under stimulation either by photons or by solvated electrons[21] might be due to slowness in any of several steps or to high reactivity in competing steps leading to termination. Inasmuch as arylation stimulated by solvated electrons fails, the problem is not primarily in the initiation step. Maybe the anions of β-dicarbonyl compounds are insufficiently nucleophilic to combine fast enough with phenyl radicals (step 3) to maintain the propagation cycle in competition with termination steps. Or maybe they interact primarily by electron transfer, in the manner of step 6, leading to termination.

It is noteworthy that numerous instances of *aliphatic* $S_{RN}1$ reactions involving the anions of β-dicarbonyl compounds as nucleophiles have been recorded by Kornblum and co-workers.[15,22]

Behavior of Methoxyacetone Enolate Ions. Methoxyacetone in principle can form three enolate ions, **10**, **11**, and **12**.



10



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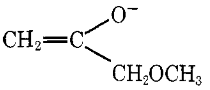
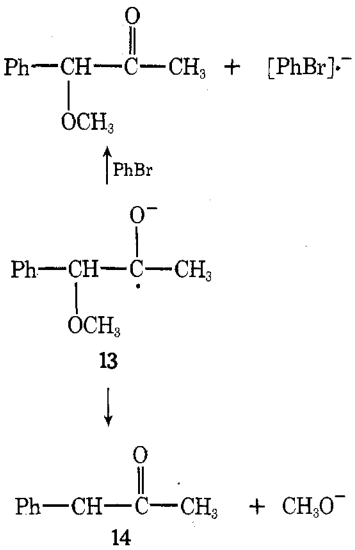


12

In expt 8, Table I, we obtained at most 0.9% of a product possibly 1-phenyl-1-methoxy-2-propanone, which would derive from **10** and/or **11**; the main product was 17% of phenylacetone (**2**), which probably stems from the same enolate ions. Combination of phenyl radical with **10** or **11** would form **13**. Electron transfer from **13** to bromobenzene (eq 11a) would afford 1-phenyl-1-methoxy-2-propanone. However, **13** appears to react preferentially by expulsion of methoxide ion, generating radical **14**. Acquisition of a hydrogen atom by the latter, either directly, perhaps by abstraction from methoxide ion,[23] or indirectly by taking an electron and then a proton, gives **2**, the observed product. Somehow the transformation of **14** to **2** must give rise to radical by-products. If the latter engage mainly in termination, the sluggishness of the overall reaction finds explanation.



(11a)

(11b)

The suggested fragmentation of **13** in reaction 11b resembles the fragmentation of phenylacetonitrile radical anion into benzyl radical and cyanide ion.[24]

Experimental Section

General. Reactants were commercial products, sometimes redistilled, whose purity was verified to exceed 99% by GLC analysis. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer, NMR spectra on a Varian A56/60A or Jeolco Minimar (60 MHz) instrument, and mass spectra on a Hitachi RMU-6E mass spectrometer. Elemental analyses were by Micro-Tech Laboratories, Skokie, Ill. Analytical gas–liquid partition chromatography (GLC) was performed with a Hewlett-Packard Model 5751B chromatograph equipped with flame ionization detector, and product isolation by GLC on a Varian Aerograph A90-P3 instrument with thermal conductivity detector. Columns of either 10% SE-54 silicone rubber or 10% Carbowax 20M on Chromosorb P were used, with helium as carrier gas throughout. Appropriate internal standards were used in analytical GLC work.

Typical Procedure. A three-necked flask (1 l.) was provided with a large cold-finger type condenser (containing solid CO_2 in 2-propanol in its central well) and a nitrogen inlet, and the stoppered third opening was used for additions. The flask was flushed with nitrogen and 240 ml of ammonia was distilled from sodium into it. Magnetic stirring was commenced, and commercial potassium *tert*-butoxide (3.65 g, 0.0325 mol) was added. The mixture was cooled to −70 °C by an external bath of solid CO_2 in 2-propanol, and 2.94 g (0.030 mol) of redistilled cyclohexanone was added. Redistilled bromobenzene (1.57 g, 0.010 mol) was added, and the entire assembly was placed in a Rayonet Model RPR-100 photochemical reactor equipped with 16 "350-nm" lamps and irradiated, with stirring, for 60 min but with interruption every 20 min to wipe accumulated frost from the outside of the flask. The flask was removed from the reactor, excess NH_4NO_3 was added and then 100 ml of diethyl ether, and the ammonia was allowed to evaporate through a condenser of the same type whose central well contained 2-propanol held at about −20 °C by occasional addition of pieces of solid CO_2. (The purpose was to ensure the retention of any benzene formed.) Water was added, the mixture was extracted with ether, and the ether layer was dried over anhydrous $MgSO_4$ and examined by GLC.

In general, if only the anticipated product was indicated to be present, the ether solution was concentrated by evaporation, the residue was distilled at reduced pressure, and the yield of purified product was determined by weighing. If a mixture was indicated, one or more internal standards was added in weighed amount and yields of the several constituents were determined by GLC; then the ether was removed by evaporation and pure samples of the products were isolated from the residue by preparative GLC. In many cases the aqueous layer remaining after ether extraction was acidified with nitric acid and analyzed for halide ion by potentiometric titration with $AgNO_3$.

Product Identification. Products were identified by their physical properties, and evidence for the main products from the tabulated reactions is now described.

Expt 3. 3,3-Dimethyl-1-phenyl-2-butanone: bp 65–66 °C (0.2 Torr); NMR (CCl_4) δ 1.12 (s, 9), 3.70 (s, 2), 7.23 (s, 5); ir (film) 700, 729, 1060, 1360, 1450, 1475, 1490, 1600, 1710, 2890–3100 cm^{-1}; MS *m/e* 176 (M^+, 10), 91 (98, benzyl?), 85 (100, trimethylacetyl?). **1,1-Diphenyl-3,3-dimethyl-2-butanone:** mp 123–126 °C; NMR (CCl_4) δ 1.12 (s, 9), 5.46 (s, 1), 7.17 (s, 10); MS *m/e* 252 (M^+, 10), 167 (100, benzhydryl?), 152 (biphenylene?), 85 (27, trimethylacetyl?), 57 (30, *tert*-butyl?).

Expt 4. 2-Phenyl-3-pentanone: bp 92–94 °C (4.0 Torr); NMR (CCl_4) δ 0.90 (t, 3), 1.33 (d, 3), 2.29 (q, 2), 3.68 (q, 1), 7.19 (s, 5); this agrees with NMR data reported by Gough et al.[25]

Expt 5 and 6. 2,4-Dimethyl-2-phenyl-3-pentanone: MS *m/e* 190 (M^+, 10), 147 (12, phenyldimethylacetyl?), 119 (100, cumyl?), 77 (80, phenyl?), 71 (dimethylacetyl?); ir (film) 704, 748, 992, 1032, 1350, 1370, 1450, 1703, 2880–3100 cm^{-1}. **2,4,4,5,5,7-Hexamethyl-3,6-octanedione:** NMR (CCl_4) δ 0.83 (d, 12), 1.03 (s, 12), 3.03 (m, 2); ir (film) 992, 1018, 1088, 1380, 1460, 1700, 2850–3000 cm^{-1}, identical with that of an authentic specimen prepared after Ansell et al.[18]

Expt 7. 3-Phenyl-4-heptanone: bp 77–81 °C (0.08 Torr); NMR (CCl_4) δ 0.76 and 0.79 (overlapping triplets, 6), 1.15–2.15 (several small peaks, 4), 2.26 (t, 2, J = 6.2 Hz), 3.44 (t, 1, J = 7.0 Hz), 7.22 (s, 5); ir (film) 701, 757, 1020, 1130, 1350, 1370, 1450, 1490, 1600, 1710, 2880–3100 cm^{-1}; MS *m/e* 190 (M^+, 100), 119 (85, phenylpropyl?), 91 (benzyl?), 71 (butyryl?), 69.5 (metastable, attributed to *m/e* 119 → 91[26]).

Expt 8. Phenylacetone was identified by the match of its NMR spectrum with that of an authentic specimen. The MS of the material responsible for a minor GLC peak of relatively long retention time indicated the presence of some 1-methoxy-1-phenyl-2-propanone (*m/e* 164) and substantial contamination by phenylacetone (*m/e* 134).

Expt 9 and 10. 2-Mesityl-3-pentanone: NMR (CCl_4) δ 0.83 (t, 3, J = 7.5 Hz, H-5), 1.20 (d, 3, J = 7.5, H-1), 2.02 (q, 2, H-4) overlapped by 2.06 (s, 9, aryl CH_3's), 3.63 (q, 1, H-2), 6.57 (s, 2, aryl H); ir (film) 848, 1050, 1450, 1708, 2885–3000 cm^{-1}; MS *m/e* 204 (M^+, 10), 147 (100, mesitylethyl?), 91 (7, benzyl?), 57 (7, propionyl?). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.96; H, 9.93.

Expt 11. 2-Phenylcyclobutanone. The ir spectrum agreed with that reported by Crandall and Conover.[27]

Expt 12. 2-Phenylcyclopentanone: ir absorption at 1740 cm^{-1} was observed, in agreement with Mislow and Hamermesh;[28] MS *m/e* 160 (M^+, 33), 117 (10, cinnamyl?), 104 (100, styrene?), 91 (12, benzyl?), 78 (10, benzene?), 77 (9, phenyl?), 58.5 (metastable, attributed to *m/e* 104 → 78[26]).

Expt 13. 2-Phenylcyclohexanone. The ir spectrum matched the published spectrum.[29a]

Expt 14. 2-Phenylcycloheptanone. The ir spectrum matched the published spectrum.[29b]

Expt 15. 2-Phenylcyclooctanone: bp 115–120 °C (0.4 Torr); NMR (CCl_4) δ 1.4–2.7 (m, 12), 3.64 and 3.83 (two doublets, 1), 7.33 (s, 5); ir (film) 700, 732, 744, 844, 1154, 1190, 1330, 1445, 1490, 1700, 2870–3100 cm^{-1}. The two NMR doublets and the 1700-cm^{-1} ir carbonyl signal agree with a report by Sisti.[30] MS *m/e* 202 (M^+, 17), 117 (87, cinnamyl?), 104 (100, styrene?), 98 (58, cyclohexanone?), 91 (77, benzyl?).

Expt 16. 1-Phenyl-2-indanone. The ir spectrum agreed with that reported by Bordwell and Scamehorn.[31] MS *m/e* 208 (M^+, 61), 178 (100, phenylbenzocyclobutadiene?), 165 (56, phenylbenzocyclopropenyl?), 152 (19, biphenylene?), 115 (13, indenyl?), 104 (47, styrene?).

Reaction of Potassium Acetone Enolate with Excess Bromobenzene. The reaction was conducted in the usual way except that bromobenzene (0.15 M) was in excess over the enolate reagent (0.05 M). Irradiation was for 120 min. Obtained were phenylacetone (32%, by GLC) and 1,1-diphenyl-2-propanone (58%, isolated and weighed). The ir spectrum of the latter matched the published spectrum.[29c]

Reaction of the Dianion of 2,4-Pentanedione with 2-Bromomesitylene. Into about 200 ml of liquid ammonia, 2.35 g (0.06 mol) of potassium metal was introduced and then a little powdered ferric nitrate. After the blue color had disappeared, 3.00 g (0.030 mol) of 2,4-pentanedione was added with stirring, and then 1.99 g (0.010 mol) of 2-bromomesitylene. The mixture was irradiated for 120 min in the photochemical reactor. The product, 1-mesityl-2,4-pentanedione, was isolated by standard procedures: bp 100–105 °C (0.3 Torr); mp 43.5–45 °C; NMR (CCl_4) δ 1.86 (s, 3), 2.16 (s, 9), 3.47 (s, 2), 5.01 (s, 2), 6.67 (s, 2); ir (film) 780, 853, 1234, 1440, 1610, 1705, 2870–3030 cm^{-1}; MS *m/e* 218 (M^+, 60), 200 (40), 160 (50), 141 (35), 134 (98), 133 (100), 119 (80). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.95; H, 8.42.

Registry No.—1, 25088-58-8; **5**, 51513-36-1; bromobenzene, 108-86-1; iodobenzene, 591-50-4; mesityl bromide, 576-83-0; mesityl iodide, 4028-63-1; 3,3-dimethyl-1-phenyl-2-butanone, 6721-67-1; 1,1-diphenyl-3,3-dimethyl-2-butanone, 58343-20-7; 2-phenyl-3-pentanone, 16819-77-5; 2,4-dimethyl-2-phenyl-3-pentanone, 25097-60-3; 3-phenyl-4-heptanone, 58343-21-8; 2-mesityl-3-pentanone, 58343-22-9; 2-phenylcyclopentanone, 1198-34-1; 2-phenylcyclooctanone, 14996-79-3; 1-phenyl-2-indanone, 24017-08-1.

References and Notes

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(2) Based in part on the Dissertation of J. E. Sundberg, University of California, Santa Cruz, June 1975.
(3) Presented in part at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975.
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