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species, such initial reaction could occur from either singlet or triplet excited states. Work aimed at elucidating the detailed nature of the ground and excited state dynamics is currently in progress.

## 4. Experimental Section

**General Procedures.** Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer. The spectra of solid samples were obtained in KBr pellets. Solution spectra were solvent-subtracted and were obtained in NaCl cells. $^1$H NMR spectra were determined on a Varian XL-300 instrument at 300 MHz using TMS as the internal standard. Ultraviolet absorption spectra were measured on a Perkin-Elmer Lambda-4 apparatus with data acquisition and processing carried out with the Perkin-Elmer PECUV software. Capillary GLC analyses were performed on a Hewlett-Packard 5890 A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3392 A integrator. Spectral-grade solvents obtained from BDH were dried by refluxing them with metallic sodium, calcium hydride, or phosphorous pentoxide as appropriate.

**Analytical Photolyses.** Solutions of acid/ester **2** (1 mL) in 3-mL Pyrex tubes were degassed by at least three freeze-pump-thaw cycles and photolyzed for 1 h with the output of a 450-W medium-pressure Hanovia lamp. An ethereal solution (1 mL) containing a large excess of freshly prepared diazomethane was added to the resulting mixtures after the solvents had been rotary evaporated to dryness. Solid samples, photolyzed in 0.4-mm i.d. Pyrex tubes both as single crystals and powders were directly dissolved in the diazomethane solution. In all cases, the diazomethane-acid mixtures were allowed to stand overnight and then analyzed by GLC.

**Quantum Yields.** Quantum yields of product formation in benzene were measured in duplicate at concentrations of **2** of $3 \times 10^{-3}$ and $10^{-2}$ M. Photolyses were carried out in a temperature-controlled water bath with the filtered 313-nm line of the medium-pressure Hanovia lamp. The formation of acetophenone by type II cleavage of 0.1 M valerophenone solutions was measured in parallel irradiations for actinometric purposes.[10] The samples were carefully degassed by repeated freeze-pump-thaw cycles and photolyzed under a positive nitrogen atmosphere.

**2-Propyl 12-Carboxy-9,10-ethenoanthracene-11-carboxylate (Dibenzobarrelene 2).** Dibenzobarrelene dicarboxylic acid anhydride (5 g, 18.3 mmol), prepared by the method of Diels and Alder,[5] was suspended in 50 mL of freshly distilled 2-propanol and refluxed for 4 h. The excess 2-propanol was evaporated from the resulting solution and the solid residue recrystallized from a mixture of acetonitrile-hexane to yield 6.05 g (99%) of the title compound: mp 176-77 °C; IR (KBr pellet) 3400-2200, 1724, 1680, 1625, 1202 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.50-6.90 (m, 8 H), 6.15 (s, 1 H), 5.78 (s, 1 H), 5.20 (hept, 1 H, $J$ = 7 Hz), 1.40 (d, 6 H, $J$ = 7Hz); HRMS (EI) $m/e$ for $C_{21}H_{18}O_4$ calcd 334.1205, found 334.1204.

**Preparative Photolysis of Dibenzobarrelene Acid/Ester 2.** A solution containing 200 mg (0.6 mmol) of **2** in 200 mL of acetonitrile was photolyzed in an immersion well for 12 h with the Pyrex-filtered output of the 450-W Hanovia lamp. Nitrogen was bubbled through the solution for 15 min before and during the photolysis period. The solvent was rotary evaporated, and an excess of diazomethane was directly distilled onto the photolysis residue. After standing for 12 h, the resulting mixture was chromatographed (silica gel, petroleum ether:EtOAc = 19:1) to yield 145 mg (70%) of a colorless oil containing a mixture of compounds **5** and **6**. Separation of **5** and **6** could be achieved in low yield by fractional recrystallization from diethyl ether.

**8c-Methyl 8b-(2-propyl) 4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8c,8b-dicarboxylate (5):** mp 139-141 °C; IR (KBr pellet) 1735, 1253 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.35-7.05 (m, 8 H), 5.24 (m, 1 H), 5.05 (s, 1 H), 4.45 (s, 1 H), 3.70 (s, 3 H), 1.32 (d, 3 H, $J$ = 7 Hz), 1.30 (d, 3 H, $J$ = 7 Hz); MS (EI) 348, 306, 260, 202. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79, found: C, 75.90; H, 5.93.

**8b-Methyl 8c-(2-propyl) 4b,8b,8c,8d-tetrahydrodibenzo[*a*,*f*]cyclopropa[*cd*]pentalene-8c,8b-dicarboxylate (6):** mp 110-112 °C; IR (KBr pellet) 1737, 1717, 1248 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.35-7.05 (m, 8 H), 5.07 (s, 1 H), 5.05 (m, 1 H), 4.49 (s, 1 H), 3.88 (s, 3 H), 1.22 (d, 3 H, $J$ = 7 Hz), 1.20 (d, 3 H, $J$ = 7 Hz); MS (EI) 348, 316, 261, 202. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79, found: C, 75.90; H, 5.93.

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# Differences in Reactivity of Stabilized Carbanions with Haloarenes in the Initiation and Propagation Steps of the $S_{RN}1$ Mechanism in DMSO

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The photostimulated reaction of acetone (2), acetophenone (5), and anthrone (8) enolate ions with iodobenzene (1) in DMSO gave good yields of substitution products by the $S_{RN}1$ mechanism. On the contrary, the monoanions of acetylacetone, diethyl malonate, and nitromethane (10) did not react under irradiation. However, the photostimulated reaction of 1 with 10 in the presence of 2 or pinacolone enolate ions gave 1-phenyl-2-nitroethane as a substitution product. The formation of this product can be explained if one assumes that the radical anion formed in the coupling reaction of phenyl radical with 10 fragments to give benzyl radical and nitrite ion. Benzyl radical then couples with 10 to give ultimately the observed product. From competition experiments the relative reactivity determined for the coupling reaction of different anions with phenyl radicals in the propagation cycle of the $S_{RN}1$ mechanism is as follows: monoanion of $\beta$ dicarbonyl compounds (unreactive) $\ll$ 2 (1.0) < 5 (7.5) < 8 (16.5). The difference in reactivity observed experimentally is explained on the basis of the p$K_a$ (HOMO energy) of the anions and on the change in the $\pi$ energy that takes place in the coupling reaction. With reference to the initiation step (electron transfer from the carbanion to 1), the reactivity increases as the p$K_a$ of the conjugated acid of the nucleophile increases.

The radical mechanism of aromatic nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on a nonactivated adequately substituted substrate.[1] The propagation steps are shown

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in eqs 1–3.

$$(\mathrm{RX})^{\bullet -} \rightarrow \mathrm{R}^{\bullet} + \mathrm{X}^{-} \qquad (1)$$

$$\mathrm{R}^{\bullet} + \mathrm{Nu}^{-} \rightarrow (\mathrm{RNu})^{\bullet -} \qquad (2)$$

$$(\mathrm{RNu})^{\bullet -} + \mathrm{RX} \rightarrow (\mathrm{RX})^{\bullet -} + \mathrm{RNu} \qquad (3)$$

Although certain carbanions have been found to be efficient nucleophiles in $S_{RN}1$ reactions with aryl halides,[1] stabilized carbanions such as the enolate ions of acetophenone[2a] or the anions of $\alpha,\beta$ unsaturated ketones[2] were found to be unreactive toward halobenzenes under photostimulation in liquid ammonia. A similar behavior was determined for the reaction of acetophenone anion with 1-chloronaphthalene.[3] This enolate ion was shown to react with iodobenzene in liquid ammonia only under drastic irradiation conditions to give 67% yield of $\alpha$-phenylacetophenone.[4] On the other hand, 2-naphthyl methyl ketone[5] and acetophenone[6–10] enolate ions react in liquid ammonia with more electrophilic substrates.

A similar behavior was reported for the reaction of monoanions of $\beta$-dicarbonyl compounds. These anions were reported not to react under photostimulation with phenyl[2a] or 2-quinolyl[6] radicals, although the 1,3-dianions of $\beta$-diketones reacted quite well through the terminal carbanion site.[2,11] Good yields of substitution were reported for the reactions of monoanions derived from $\beta$-dicarbonyl or $\beta$-cyanocarbonyl compounds with more electrophilic substrates.[12,13]

Recently, it has been found that aromatic azosulfides with electron-withdrawing groups react with the monoanions of $\beta$-dicarbonyl compounds although phenyl, 2-naphthyl, and *p*-anisyl azosulfides react sluggishly.[14]

The anions from nitroalkanes have been shown by different techniques (ESR,[15] optical absorption spectra,[16] and electrochemical studies[17]) to be very good traps for aryl and alkyl radicals. However, the radical anion formed in the coupling of an aryl radical with nitromethane anion fragments faster than the electron transfer (eq 4), producing stable benzyl radicals; this accounts for the lack of photostimulated or metal-promoted reactions of this type.[18]

$$\mathrm{Ar}^{\bullet} + {}^{-}\mathrm{CH2NO2} \rightarrow (\mathrm{ArCH2NO_2})^{\bullet -} \rightarrow \mathrm{ArCH_2}^{\bullet} + \mathrm{NO_2}^{-} \qquad (4)$$

**Table I. Photostimulated Reactions of Iodobenzene with Carbanions in DMSO**[a]

| expt | PhI (mmol) | ketone (mmol) | *t*-BuOK (mmol) | $X^-$ | substn products[b] (%) |
|---|---|---|---|---|---|
| 1[c] | 2.45 | $CH_3COCH_3$ (20.0) | 22.6 | 99 | $CH_3COCH_2Ph$ (88)<br>$CH_3COCHPh_2$ (11) |
| 2 | 1.06 | $PhCOCH_3$ (3.0) | 3.4 | 79 | $PhCOCH_2Ph$ (68)<br>$PhCOCHPh_2$ (13) |
| 3[d] | 1.03 | $PhCOCH_3$ (3.0) | 3.4 | ≤1 | |
| 4[e] | 1.03 | $PhCOCH_3$ (3.0) | 3.5 | 15 | $PhCOCH_2Ph$ (13) |
| 5 | 1.06 | $PhCOCH_3$ (3.0)<br>$CH_3COCH_3$ (3.0) | 6.9 | 98 | $PhCOCH_2Ph$ (76)<br>$PhCOCHPh_2$ (11)<br>$PhCH_2COCH_3$[f] |
| 6 | 1.04 | $CH_3COCH_2COCH_3$ (3.0) | 3.5 | 12 | *g* |
| 7 | 1.04 | $CH_3COCH_2COCH_3$ (3.0)<br>$CH_3COCH_3$ (1.5) | 5.0 | 91 | $PhCH_2COCH_3$ (34)<br>$Ph_2CHCOCH_3$ (28) |
| 8 | 1.96 | $CH_2(CO_2Et)_2$ (6.0) | 7.9 | 12 | *g* |
| 9 | 1.03 | anthrone (2.0) | 2.9 | 98 | 10-Ph-anthrone (95) |
| 10[d] | 1.03 | anthrone (2.0) | 2.9 | ≤1 | |
| 11[e] | 1.03 | anthrone (2.0) | 2.9 | 64 | 10-Ph-anthrone (60) |
| 12 | 1.88 | $CH_3NO_2$ (6.0) | 7.0 | 0 | |
| 13 | 1.23 | $CH_3NO_2$ (3.0)<br>$CH_3COCH_3$ (1.5) | 5.0 | 26 | $PhCH_2CH_2NO_2$ (11)<br>PhH (2); $PhCH_3$ (1) |
| 14 | 1.03 | $CH_3NO_2$ (3.0)<br>$Me_3CCOCH_3$ (1.5) | 4.8 | 9 | $PhCH_2CH_2NO_2$;[f]<br>$PhCH_3$ |
| 15 | 1.03 | $CH_3NO_2$ (3.0)<br>$PhCOCH_3$ (2.0) | 5.9 | 10 | *f* |
| 16[h] | 1.03 | $CH_3NO_2$ (3.0)<br>$Me_3CCOCH_3$ (1.5) | 5.1 | 48 | NaphH (6)<br>1-MeNaph (10)<br>(1-Naph)$CH_2CH_2NO_2$ (10) |
| 17[i] | 0.98 | $CH_3NO_2$ (3.0)<br>$Me_3CCOCH_3$ (1.5) | 5.0 | 93 | benzophenone (2)<br>4-Me-benzophenone (22) |
| 18[d,i] | 0.98 | $CH_3NO_2$ (3.0)<br>$Me_3CCOCH_3$ (1.5) | 5.0 | 91 | benzophenone (2)<br>4-Me-benzophenone (20) |
| 19[d,e,i] | 0.97 | $CH_3NO_2$ (3.0)<br>$Me_3CCOCH_3$ (1.5) | 5.0 | 31 | benzophenone (1)<br>4-Me-benzophenone (11) |

[a] Reactions carried out in 25 mL of DMSO and irradiated during 120 min, unless otherwise indicated. [b] Quantified by GLC, unless otherwise indicated. [c] Irradiation time: 60 min. [d] Dark reaction. [e] *p*-Dinitrobenzene (20 mol %) was added. [f] Detected, but not quantified. [g] Product not detected. [h] Substrate 1-iodonaphthalene. [i] Substrate 4-bromobenzophenone.

It has been reported that 1-iodoadamantane[19a] and *tert*-butylmercury chloride[19b] react easily with stabilized carbanions, including nitromethane anion, by the $S_{RN}1$ mechanism in DMSO. These facts prompted us to investigate the photostimulated reaction of stabilized carbanions with haloarenes in this solvent in order to determine the structure–reactivity relationship that governs the reaction.[20]

## Results

**Ketone Enolate Ions.** In the photostimulated reaction of iodobenzene (1) with acetone enolate ion (2), after 60 min of irradiation, we obtained phenylacetone (3) (88% yield) and 1,1-diphenylacetone (4) (11% yield) (eq 5) (Table I, experiment 1).

$$\underset{1}{\mathrm{PhI}} + \underset{2}{{}^{-}\mathrm{CH_2COCH_3}} \xrightarrow{h\nu} \underset{3}{\mathrm{PhCH_2COCH_3}} + \underset{4}{\mathrm{Ph_2CHCOCH_3}} \qquad (5)$$

The photostimulated reaction (120 min) of 1 and the enolate ion of acetophenone (5) gives the substitution product $\alpha$-phenylacetophenone (6) (68% yield) and $\alpha,\alpha$-

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**Table II. Competition Experiments between Carbanions toward Iodobenzene in DMSO**[a]

| expt | ketones (mmol) | *t*-BuOK (mmol) | $X^-$ | substn products[b] (%) | rel reactivity |
|---|---|---|---|---|---|
| 1 | **8** (1.99); **5** (3.00) | 5.94 | 81 | **9** (48); **6** (34) | $k_8/k_5 = 2.2$ |
| 2 | **8** (1.99); **5** (4.02) | 6.96 | 85 | **9** (44); **6** (44) | $k_8/k_5 = 2.1$ |
| | | | | | Avg $k_8/k_5 = 2.2 \pm 0.05$ |
| 3 | **5** (1.97); **2** (3.94) | 6.96 | 97 | **6** (77);[c] **3** (25) | $k_5/k_2 = 7.7$ |
| 4 | **5** (1.97); **2** (5.02) | 7.84 | 95 | **6** (68);[d] **3** (28) | $k_5/k_2 = 7.4$ |
| | | | | | Avg $k_5/k_2 = 7.5 \pm 0.2$ |
| 5 | **5** (4.96); **10** (3.02)[e] | 12.9 | 20 | **6** (13); **11** (8) | $k_5/k_{10} = 1$ |
| 6 | **5** (4.96); **10** (2.60)[e] | 13.0 | 20 | **6** (16); **11** (9) | $k_5/k_{10} = 0.9$ |
| | | | | | Avg $k_5/k_{10} \approx 1$ |

[a] Reactions carried out in 25 mL of DMSO with 1.03 mmol of iodobenzene and irradiated during 120 min. [b] Quantified by GLC. [c] Combinated yields of **6** (60%) and **7** (17%). [d] Combinated yields of **6** (56%) and **7** (12%). [e] Acetone: 3.94 mmol.

diphenylacetophenone (**7**) (13% yield) (eq 6) (Table I, experiment 2).

$$1 + \underset{\mathbf{5}}{{}^-CH_2COPh} \xrightarrow{h\nu} \underset{\mathbf{6}}{PhCH_2COPh} + \underset{\mathbf{7}}{Ph_2CHCOPh} \qquad (6)$$

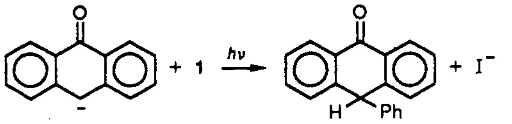
There is no reaction in the dark, and the photostimulated reaction is inhibited by *p*-dinitrobenzene (*p*-DNB) (Table I, experiments 3 and 4).

In competition experiments carried out with both **2** and **5** in equal concentration, we found higher yields of substitution product derived from **5** (Table I, experiment 5).

In the photostimulated reaction of **1** with the monoanion of acetylacetone or with the diethylmalonate anion we found only 12% yield of iodide ions but no substitution products were found (Table I, experiments 6 and 8).

In competition experiments between the monoanion of acetylacetone and **2** we found only substitution products from **2** (Table I, experiment 7), despite its concentration being half that of the monoanion of acetylacetone. This result suggests that the reactivity of **2** is higher than that of acetylacetone enolate ions.

On the other hand, in the photostimulated reaction of anthrone anion (**8**) with **1** a 95% yield of the substitution product **9** was found (eq 7) (Table I, experiment 9).



**8** **9** (7)

This reaction did not occur in the dark, and the photostimulated reaction was inhibited by *p*-DNB (Table I, experiments 10 and 11).

Once the yields of substitution products **6** and **9** were determined in the photostimulated reaction of **1** with nucleophiles **5** and **8** in excess, it was possible to calculate $k_8/k_5$ by means of eq 8.[21]

$$\frac{k_8}{k_5} = \frac{\ln [8]_0/[8]_t}{\ln [5]_0/[5]_t} \qquad (8)$$

where $[5]_0$ and $[8]_0$ are initial concentrations and $[5]_t$ and $[8]_t$ are concentrations at time *t*. This equation is based on a first-order reaction of both nucleophiles with the phenyl radicals. The $k_8/k_5$ thus determined was 2.2 ± 0.05 (Table II).

By the same procedure and with enolate ions **2** and **5** in excess we determined that nucleophile **5** is 7.5 ± 0.2 more reactive than enolate ion **2** (Table II). On the basis of these relative reactivities, $k_8/k_2$ can be estimated as 16.5.

We were unable to determine the relative reactivity of **2** compared with the monoanion of acetyl acetone because no coupling products from the latter nucleophile were obtained. This result suggests that either **2** is more reactive than the monoanion or that this latter is unable to couple with phenyl radicals.

**Nitromethane Ion.** In the photostimulated reaction of **1** and the nitromethane anion (**10**) we did not find any reaction at all (Table I, experiment 12). However, when the reaction was carried out in the presence of **2** or pinacolone enolate ions, we found 1-phenyl-2-nitroethane (**11**) as major product, together with small amounts of benzene and toluene (Table I, experiments 13 and 14) (eq 9). No products from the coupling with ketone enolate ions were found.

$$1 + \underset{\mathbf{10}}{{}^-CH_2NO_2} + {}^-CH_2COR \xrightarrow{h\nu} \underset{\mathbf{11}}{PhCH_2CH_2NO_2} + PhH + PhCH_3 \qquad (9)$$

$$R = CH_3,\ t\text{-butyl}$$

We suggest that this reaction follows the $S_{RN}1$ mechanism, but the coupling reaction of phenyl radical with **10** gave a radical anion intermediate that fragments (eq 4, Ar = Ph) giving benzyl radicals (**12**). These are reduced to toluene or react with **10** to give a new radical anion **13** (eq 10), which now transfers the electron to **1** (eq 11) to give the substitution product **11**.

$$\underset{\mathbf{12}}{PhCH_2^{\bullet}} + \mathbf{10} \rightarrow \underset{\mathbf{13}}{(PhCH_2CH_2NO_2)^{\bullet-}} \qquad (10)$$

$$\mathbf{13} + PhI \rightarrow \underset{\mathbf{11}}{PhCH_2CH_2NO_2} + (PhI)^{\bullet-} \qquad (11)$$

The radical anion **13** does not fragment in the sense of eq 4 because in this case a less stable nonbenzylic primary alkyl radical would be formed.

In order to try to avoid the fragmentation of the intermediate radical anion,[1a,22] reactions were carried out with substrates having a lower $\pi$ antibonding MO such as 1-iodonaphthalene (**14**) and 4-bromobenzophenone.

In the photostimulated reaction of **10** with **14** in the presence of pinacolone ion we found only 48% yield of iodide ions, naphthalene, 1-methylnaphthalene, and 1-(1-naphthyl)-2-nitroethane (**15**) as products (Table I, experiment 16) (eq 12).

$$\underset{\mathbf{14}}{\text{1-I-Naph}} + \mathbf{10} + {}^-CH_2COC(Me)_3 \xrightarrow{h\nu} \underset{\mathbf{15}}{(\text{1-Naph})CH_2CH_2NO_2} \qquad (12)$$

$$\text{Naph} = \text{naphthyl}$$

4-Bromobenzophenone gave a dark reaction in the presence of **10** and pinacolone enolate ions. The reaction was inhibited by *p*-DNB. In the dark as well as in the photostimulated reaction there was a poor mass balance. The only products isolated and identified were benzophenone and 4-methylbenzophenone, although in low yield (ca. 10–22%), (Table I, experiments 17–19). In the photostimulated reaction of **10** with 2-chloroquinoline, the products found were quinoline and 2-methylquinoline quantified in low yield (not reported in the table).

In competition experiments between **5** and **10** there was overall inhibition of the reaction (Table I, experiment 15).

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**Table III. Relative Reactivities, HOMO of the Carbanions, and SOMO of the Radical Anion Intermediates for the Coupling of Phenyl Radicals with Carbanions**

| carbanions derived from | rel reactivity | $pK_a$[a] | HOMO (eV) | SOMO (eV) | $\Delta E_\pi$ (HOMO-SOMO) |
|---|---|---|---|---|---|
| acetylacetone | 0 | 13.3 | −3.21 | −1.38 | 1.83 |
| acetone | 1.00 | 26.5 | −1.96 | −1.04 | 0.92 |
| acetophenone | 7.5 | 24.7 | −2.51 | −1.95 | 0.56 |
| nitromethane | (≈7.5)[b] | 17.2 | −3.08 | (−2.52)[c] | 0.56 |
| anthrone[d] | 16.5 | | −2.99 | −2.42 | 0.57 |

[a] See ref 27. [b] Aparent value. [c] Radical anion calculated with a fixed $Csp^2$(phenyl)$Csp^3$ (nitromethyl anion) bond distance. [d] Carbanion and radical anion calculated by the MNDO method, UHF version (for the sake of simplicity, in the radical anion the phenyl group was replaced by a methyl group).

This result suggests that **5** is less reactive than **2** or pinacolone enolate ions to initiate the reaction. On the other hand, **10** reacts with phenyl radicals to give a radical anion which fragments into less reactive benzyl radicals, thus decreasing the efficiency of the chain propagation step. This and the fact that **5** is less reactive to initiate the reaction could be the reason for the overall low reaction observed.

In competition reactions we found that **10** has approximately the same reactivity as **5** ($k_{10}/k_5 \approx 1$) (Table II).

## Discussion

The facts that carbanions **2**, **5**, **8**, and **10** (in the presence of good electron donors, such as **2**) react under irradiation in DMSO and that their photostimulated reactions are inhibited by *p*-DNB suggest that these reactions occur by the $S_{RN}1$ mechanism. Qualitatively, **2** is more reactive than **5** in separated experiments, but in competition experiments **5** is 7.5 more reactive than **2**. Carbanion **8** reacts 2.2 times faster than **5** (thus **8** reacts 16.5 times faster than **2**). In competition experiments between **2** and acetylacetone enolate ions no substitution product from the latter could be found. Moreover, **10**, one of the less reactive nucleophiles by itself, like monoanions of $\beta$ dicarbonyl compounds, reacts in the presence of good electron donors and it has an apparent reactivity similar to **5**.

All these results suggest that as the $S_{RN}1$ mechanism is a chain process with initiation, propagation, and termination steps, the carbanions show in the initiation step a different reactivity from that shown in the coupling reaction of the propagation cycle (eq 2).

In the initiation step, we determined qualitatively the following order of electron-transfer capability: $\mathbf{2} > \mathbf{5} \approx \mathbf{8} \gg \mathbf{10} \approx$ monoanion of acetylacetone ≈ diethyl malonate enolate ion (unreactive when initiation by light is used). This sequence follows roughly the same order of the $pK_a$ of the conjugated acids of the carbanions as has previously been proposed.[23]

On the other hand, the reactivity in the coupling reaction (eq 2) which corresponds to the reactivity determined experimentally in competition experiments does not follow the same order of the pKa of the ketones.

From a frontier orbital point of view the most important interaction in this coupling reaction is between the HOMO of the nucleophile and the SOMO of the radical. As a result of this interaction a $\sigma$ and a $\sigma^*$ MO are formed. The $\sigma$ double occupied MO corresponds to the newly formed C–C bond. The extra electron of the radical anions under study will occupy the lower $\pi^*$ MO of the system (SOMO of the radical anion intermediate).

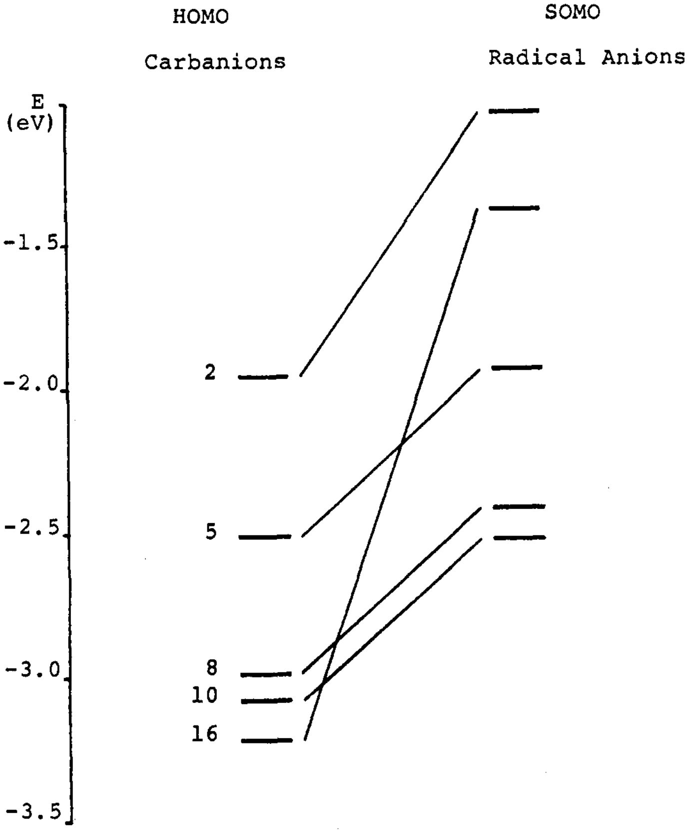

**Figure 1.** $\Delta E_\pi$ (HOMO–SOMO) in the coupling reaction of phenyl radicals with carbanions.

In Table III the HOMO energy of the carbanions and SOMO energy of the corresponding radical anions are presented. These values were calculated by the AM1 method, UHF version, as implemented in AMPACK.[24]

As can be seen the HOMOs of the calculated carbanions become lower in energy as the $pK_a$ of the corresponding conjugated acids decrease, which corresponds to an increase of the oxidation potentials as determined experimentally.[25]

From inspection of Table III neither the stability of the radical anions formed in the coupling step (measured through the energy of their SOMO) nor the $pK_a$ of the conjugated acids of the nucleophiles (measured through the energy of their HOMO) explain the reactivity observed.

Previous studies tried to correlate the rate of the coupling reaction with the overall change in free energy, which for a series of anions with resulting radical anions of similar stability should increase with the $pK_a$ of the conjugate acid of the anion. In these systems an inverted reactivity order as a function of $pK_a$ or $\Delta G°$ was determined.[19b,26]

A similar behavior has been observed for our system in which the radical anions obtained have different stability. Changing the $pK_a$ from 26.5 (acetone)[27] to 24.7 (acetophenone)[27] increases the reactivity by 7.5. For anthrone anion, with a HOMO of lower energy than **2** or **5** and thus a lower $pK_a$, the reactivity increases by 16.5 compared with **2**.

With acetylacetonate ion, the nucleophile studied with lower HOMO and lower $pK_a$ value, no substitution reaction could be determined.

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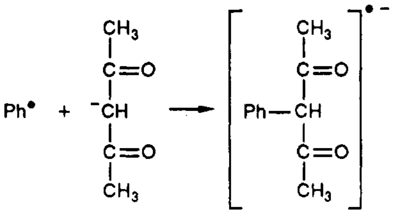
Analyzing the HOMO energy of the anions and the SOMO energies of the corresponding radical anions, we propose that the rate of the coupling reaction depends on the $pK_a$ of the conjugated acids as well as on the HOMO–SOMO energy difference which can be considered as an indication of the loss in $\pi$ energy of the system.

For **2**, **5**, and **8** the HOMO of the anions and the SOMO of the corresponding radical anions follow the same order (see Figure 1). This is so because the features of the structures that determine the $pK_a$ of the conjugated acids of **2**, **5**, and **8** determine the SOMO energy of the corresponding radical anions. With these carbanions the reactivity increases with a decrease in the $pK_a$ of the conjugated acids or with a decrease in energy of their HOMOs and SOMOs.

The monoanions of $\beta$ dicarbonyl compounds, such as acetylacetonate anion, were expected to be highly reactive on the basis of their $pK_a$; however, the HOMO–SOMO energy difference for the system was higher than for the other anions. For this type of nucleophile the structure **16** that determines the $pK_a$ (two conjugated carbonyl groups) changes considerably in the radical anion intermediate **17** in which the two carbonyl groups are separated by an $sp^3$ carbon atom; thus, conjugation no longer exists between them (eq 13).


16 17 (13)

This fact produces a large HOMO–SOMO energy difference (an important loss in $\pi$ energy, see Figure 1). This effect is sufficiently important to retard the reaction, and these carbanions do not couple with phenyl radicals.

However, nitromethane, with a $pK_a$ of 17.2,[27] has a similar reactivity to that of **5**. This is an apparent reactivity due to the fragmentation of the radical anion formed in the coupling reaction. MO calculations show that this radical anion does not correspond to a minimum of the potential surface, the electron capture being dissociative. The process is still dissociative even when aromatic moieties with lower antibonding $\pi^*$ MO such 1-naphthyl, 4-benzoylphenyl, or 2-quinolyl are used.

## Conclusions

We conclude that the reactivity of carbanion nucleophiles in photostimulated reactions with haloaromatic compounds depends on the nature of the reaction step. Thus, in the initiation step the photostimulated electron transfer from the carbanion to the acceptor iodobenzene increases with the $pK_a$ of the corresponding conjugated acids.

In the propagation cycle the reactivity of the carbanions would depend on their $pK_a$ as well as on the SOMO of the radical anion intermediate, that is, the HOMO–SOMO energy difference (loss in $\pi$ energy).

Carbanions derived from nitroalkanes are not suitable to react with haloarenes due to the frangibility of the radical anion intermediates.

## Experimental Section

**General Method.** $^1H$ NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to $Me_4Si$ ($\delta$), with $CCl_4$ as the solvent. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik instrument with a flame ionization detector and data system Shimatzu CR-3A, using a column packed with 5% OV17 on Chromosorb G (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–270 mesh ASTM). Irradiation was conducted in a reactor equipped with two 250-W lamps emitting maximally at 350 nm (Philips Model HPT, air refrigerated). Potentiometric titration of halide ions was performed in a pH meter (Seybold Wien) using an $Ag/Ag^+$ electrode. Melting points were obtained with a Büchi 510 apparatus and are not corrected.

**Materials.** 4-Bromobenzophenone (Janssen), *tert*-butyl alcohol (Aldrich), potassium *tert*-butoxide (Fluka), iodobenzene (Aldrich), 1-iodonaphthalene (Janssen), anthrone (Carlo Erba), and 2-chloroquinoline (Fluka), were commercially available and used as received. DMSO (Carlo Erba) was distilled under vacuum and stored under molecular sieves (4 Å). Acetone (Merck) was distilled and stored under molecular sieves (4 Å). Nitromethane (Aldrich), acetylacetone (Aldrich), and diethyl malonate (Mallinckrodt) were distilled and dried over $MgSO_4$. Pinacolone was synthesized as described.[28]

**Photostimulated Reaction of Acetophenone Enolate Ion with Iodobenzene.** The following procedure is representative of these reactions. The reactions were carried out in a 100-mL three-neck round-bottomed flask equipped with nitrogen inlet and magnetic stirrer. To 25 mL of dry and degassed DMSO under nitrogen was added 3.44 mmol of potassium *tert*-butoxide, 3.0 mmol of acetophenone, and 1.06 mmol of iodobenzene. After 120 min of irradiation the reaction was quenched by adding ammonium nitrate in excess, water (50 mL), and diethyl ether (50 mL). The iodide ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water, dried, and quantified by GLC. 1-Bromonaphthalene was used as internal standard. The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel (eluted with hexane:diethyl ether = 90:10) gave $\alpha$-phenylacetophenone: mp 59–60 °C (lit.[29] mp 60 °C); $^1H$ NMR $\delta$ 4.18 (2 H, s); 7.10–7.99 (10 H, m); MS (30 eV) $m/e$ (relative intensity) 196 (18), 106 (41), 105 (100), 91 (31), 77 (67).

**1-Phenyl-2-nitroethane.**[30] Liquid isolated by column chromatography on silica gel (eluted with hexane:diethyl ether = 90:10): $^1H$ NMR $\delta$ 3.24 (2 H, t), 4.50 (2 H, t), 7.18 (5 H, s); MS (30 eV) $m/e$ (relative intensity) 254 (6), 167 (7), 151 (5), 117 (13), 105 (39), 104 (100), 91 (22), 90 (6), 77 (44), 51 (29).

**1-(1-Naphthyl)-2-nitroethane.**[31] Liquid isolated by column chromatography on silica gel (eluted with petroleum ether:diethyl ether = 90:10): $^1H$ NMR $\delta$ 3.74 (2 H, t), 4.60 (2 H, t), 7.25–8.08 (7 H, m); MS (30 eV) $m/e$ (relative intensity) 201 (20), 166 (5), 154 (100), 141 (24), 129 (16), 128 (22), 127 (23), 126 (15), 115 (28), 77 (54).

**10-Phenylanthrone.** Solid isolated by column chromatography on silica gel (eluted with petroleum ether:dichloromethane:diethyl ether = 60:30:10): mp 140 °C dec (darkness) (lit.[32a] mp 146 °C dec; lit.[32b] mp 139–140 °C dec); $^1H$ NMR $\delta$ 5.25 (1 H, s), 6.72–8.31 (13 H, m); $^{13}C$ NMR $\delta$ 54.15. 125.26 126.43, 126.60, 127.65, 128.29, 131.95, 133.55, 133.81, 139.71, 145.98, 147.7, 183.6.

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la Provincia de Córdoba and Antorchas Foundation.

**Registry No.** 1, 591-50-4; 2, 24262-31-5; 3, 103-79-7; 4, 781-35-1; 5, 34438-71-6; 6, 451-40-1; 7, 1733-63-7; 8, 91120-35-3; 9, 14596-70-4; 10, 18137-96-7; 11, 6125-24-2; 14, 27252-54-6; 15, 70360-84-8; 16, 17272-66-1; 4-bromobenzophenone, 90-90-4; acetylacetone, 123-54-6; diethyl malonate, 105-53-3; anthrone, 90-44-8; nitromethane, 75-52-5; methyl *tert*-butyl ketone, 75-97-8; acetylphenone, 98-86-2; acetone, 67-64-1; 1-methylnaphthalene, 90-12-0; 4-methylbenzophenone, 134-84-9; phenyl radical, 2396-01-2.

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# Synthesis and Properties of 4,4,9,9-Tetramethyl[12]paracyclophane-5,6,7,8-tetrone[†]

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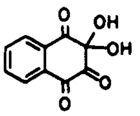
The synthesis of 4,4,9,9-tetramethyl[12]paracyclophane-5,6,7,8-tetrone (**26**) has been achieved in a multistep procedure. Compound **26** is the first cyclic tetraketone whose structure has been studied by X-ray analysis. The key intermediates were 4,4,9,9-tetramethyl[12]paracyclophane-6,7-dione (**22**), 6,7-bis[(trimethylsilyl)oxy]-4,4,9,9-tetramethyl[12]paracyclophane-5,7-diene (**24**), and two epimeric 5,8-dihydroxy-4,4,9,9-tetramethyl[12]-paracyclophane-6,7-diones **25a** and **25b**. X-ray analyses have been performed on **24**, **25b** and **26**. That on **24** reveals a dihedral angle of 57° between the two silylenol ether groups. The product analyses and the configurations of **25a** and **25b** together with the isolation of the bis(epoxide) intermediate **28** allow conclusions to be drawn on the oxidation mechanism of **24** with *m*-CPBA (Rubottom reaction). The stability of **26** is ascribed to steric factors.

Vicinal polyketones have been known for more than a century and have been well studied.[1] Although the first members of the acyclic series diphenyl triketone and diphenyl tetraketone were described nearly at the same time, in 1890[2] and 1892,[3] respectively, the properties of vicinal tetraketones were investigated much later[1,4] than those of vicinal triketones. The next higher homologue, diphenyl pentaketone,[5] was reported only recently. Data concerning cyclic polyketones are much more scarce. Before 1987, cyclic tetraketones were known only as hydrates such as 1 and 2[6] or as strong electron-donor substitutents such as the salt of rhodizonic acid (3).[7]



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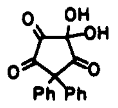

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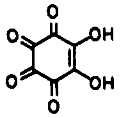

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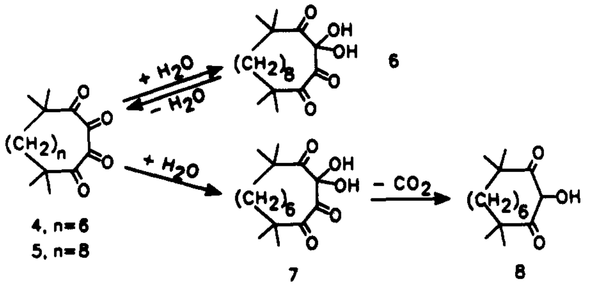
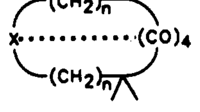
Our unsuccessful attempts to generate cyclic tetraketones from hydrates like 1, 2 or related species[8] we ascribe to the fact that the accumulation of strong local dipoles (CO) together with the electron-withdrawing effect of phenyl groups leads to kinetically and thermodynamically unstable species. The partial cancellation of local dipoles can be attained by adding a strong electron-donor fragment to the vicinal polyketone as, for example, in the oxocarbons.[7] Another possible way to achieve stability is to increase the flexibility of the cyclic system. This idea led to the syntheses of 4 and 5,[9] which were the first cyclic vicinal tetraketones isolated. It turned out that the hydrate of 5 is rather stable, whereas 4 reacts very rapidly with water accompanied by ring contraction[9] to an acireductone 8.

Another way to stabilize such cyclic tetraketones is by transannular donor–acceptor interactions as indicated in 9. The symbol X represents electron-rich atoms or groups such as O, S, NR, or π-systems. In this paper, we wish to report our efforts to synthesize a vicinal tetraketone in the [12]cyclophane series. We chose this system because molecular modeling suggested that such a chain length should provide enough flexibility to arrange the $(CO)_4$ fragment in a helical geometry, as found for most acyclic and monocyclic compounds.





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[†] Dedicated to Professor Mordecai B. Rubin on the occasion of his 65th birthday.

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