

## Electron Transfer Reactions. Reaction of Furanones and Bifurandiones with Potassium and Oxygen<sup>1)</sup>

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Received August 12, 1985

Treatment of furanones (**1a–c**, **25**, **34**) and bifurandiones (**23**, **37**) with potassium in THF gave rise to radical anion intermediates, which reacted with oxygen to give superoxide and ultimately products derived through the reaction of superoxide with the starting furanones and bifurandiones. Thus, the reaction of **1a** with potassium gave a mixture of 4-oxo-2,2,4-triphenylbutanoic acid (**7a**), 1,3,3-triphenyl-2-propen-1-one (**11a**), and benzoic acid (**12**). The reaction of **11a** itself, under similar conditions, gave a mixture of benzophenone (**18a**) and **12**. Similar reactions have been observed in the case of **1b** and **c**. The bifurandione **23**, on treatment with potassium, gave a mixture of the 2(5*H*)-furanone **25**, 2,3-diphenylpropenoic acid (**31**), and **12**. The reaction of **25** itself with potassium under similar conditions gave the same mixture of **31** and **12**. Treatment of 3-phenyl-2(3*H*)-benzofuranone (**34**) with potassium, however, did not give any isolable product; only the starting material could be recovered. Under similar conditions, the bifurandione **37** gave the fragmentation product **34**. Cyclic voltammetric studies have been employed to measure the reduction potentials, leading to radical anions, and these intermediates have been characterized through their electronic spectra.

### Elektronen-Übertragungs-Reaktionen. Reaktion von Furanonen und Bifurandionen mit Kalium und Sauerstoff<sup>1)</sup>

Bei der Behandlung von Furanonen (**1a–c**, **25**, **34**) und Bifurandionen (**23**, **37**) mit Kalium in THF entstehen Radikalanion-Zwischenstufen, die mit Sauerstoff zu Superoxid reagieren, das seinerseits mit den Ausgangsfuranonen und -bifuranonen weiterreagiert. So ergab die Reaktion von **1a** mit Kalium eine Mischung von 4-Oxo-2,2,4-triphenylbutansäure (**7a**), 1,3,3-Triphenyl-2-propen-1-on (**11a**) und Benzoesäure (**12**). Unter ähnlichen Bedingungen reagierte **11a** selbst zu einer Mischung von Benzophenon (**18a**) und **12**. Ähnliche Ergebnisse wurden im Falle von **1b** und **c** erhalten. Das Bifurandion **23** ergab mit Kalium eine Mischung von 2(5*H*)-Furanon **25**, 2,3-Diphenylpropensäure (**31**) und **12**. **25** selbst reagierte mit Kalium unter ähnlichen Bedingungen zur selben Mischung von **31** und **12**. 3-Phenyl-2(3*H*)-benzofuranon (**34**) führte mit Kalium jedoch zu keinem isolierbaren Produkt; nur Ausgangsmaterial wurde zurückgewonnen. Unter vergleichbaren Bedingungen lieferte das Bifurandion **37** das Fragmentierungsprodukt **34**. Mit Hilfe der cyclischen Voltammetrie wurden die zu den Radikalanionen führenden Reduktionspotentiale gemessen. Die Radikalanion-Zwischenstufen wurden durch ihre Elektronenspektren charakterisiert.

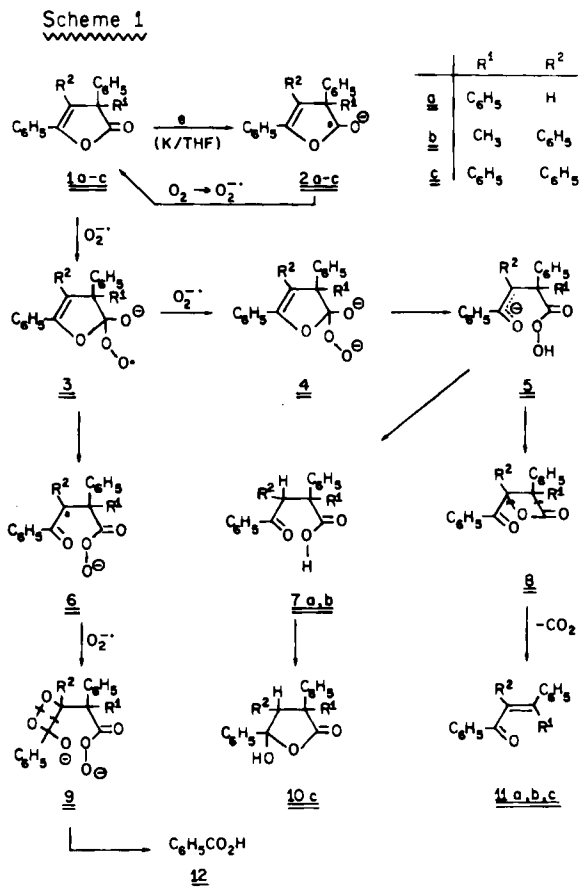
Alkali metals react with unsaturated organic compounds through electron transfer reactions to give radical anion and dianion intermediates, which in turn undergo a variety of transformations, depending on the reaction conditions<sup>3</sup>. In a recent investigation, we have shown that the reaction of a 1,2-dibenzoylalkene derivative such as 11,12-dibenzoyl-9,10-dihydro-9,10-ethanoanthracene with potassium in tetrahydrofuran (THF), for example, gives a mixture of 9,10-dihydro-12-( $\alpha$ -hydroxybenzylidene)-11-phenyl-9,10-ethanoanthracene-11-carboxylic acid, anthracene, and benzoic acid<sup>4</sup>. It has been suggested that the initially formed radical anion intermediate, in this reaction, undergoes transformation to a furanone, which ultimately leads to the products. Similar radical anion intermediates have been postulated in the potassium-induced transformations of several 1,2-dibenzoylalkenes<sup>5</sup>. In this context, it was felt worthwhile to investigate the reaction of some representative furanones and bifurandiones with potassium in THF.

## Results and Discussion

In the present studies, we have examined the reactions of 3,3,5-triphenyl-2(3*H*)-furanone (**1a**), 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone (**1b**), 3,3,4,5-tetraphenyl-2(3*H*)-furanone (**1c**), 3,4,5-triphenyl-2(5*H*)-furanone (**25**), and 3-phenyl-2(3*H*)-benzofuranone (**34**). In addition, the reaction of two bifurandiones such as 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5'(2*H*,2'*H*)-dione (**23**), and 3,3'-diphenyl-3,3'-bibenzofuran-2,2'(3*H*,3'*H*)-dione (**37**) have also been examined.

The reaction of **1a** with potassium in THF (10 h), for example, gave a mixture of 4-oxo-2,2,4-triphenylbutanoic acid (**7a**), 1,3,3-triphenyl-2-propen-1-one (**11a**), and benzoic acid (**12**). Similar product mixtures consisting of **7a**, **11a**, and **12** were obtained with **1a** and potassium after 20 h, under analogous conditions, with **1a** and excess potassium, and also when the reaction mixture was saturated with oxygen before workup. However, in the cases with a longer reaction time (20 h) and under oxygen saturation, higher yields of benzoic acid (**12**) were observed. Similarly, the reaction of **1b** with potassium in THF gave a mixture of 2-methyl-2,3,4-triphenylbutanoic acid (**7b**) and 1,2,3-triphenyl-2-buten-1-one (**11b**). In a separate experiment, when the reaction mixture from **1b** was saturated with oxygen before workup, a mixture of **7b**, **11b**, and benzoic acid (**12**) was obtained. The reaction of **1c** with potassium in THF, likewise, gave a mixture of 4,5-dihydro-5-hydroxy-3,3,4,5-tetraphenyl-2(3*H*)-furanone (**10c**), 1,2,3,3-tetraphenyl-2-propen-1-one (**11c**), and benzoic acid (**12**). A similar product mixture consisting of **10c**, **11c**, and **12** was obtained when the reaction mixture from **1c** was saturated with oxygen before workup. The structures of all the products were determined on the basis of analytical results, spectral data, and comparison with authentic samples, wherever known. The structure of **10c**, for example, was confirmed through its conversion to the furanone **1c**, on treatment with HCl gas in THF.

The formation of the different products in the reaction of **1a**–**c** with potassium in THF could be understood in terms of the pathway shown in Scheme 1. It has been assumed that the initial step in the reaction of **1** with potassium is an electron transfer process, leading to the radical anion intermediate **2**, which can then react

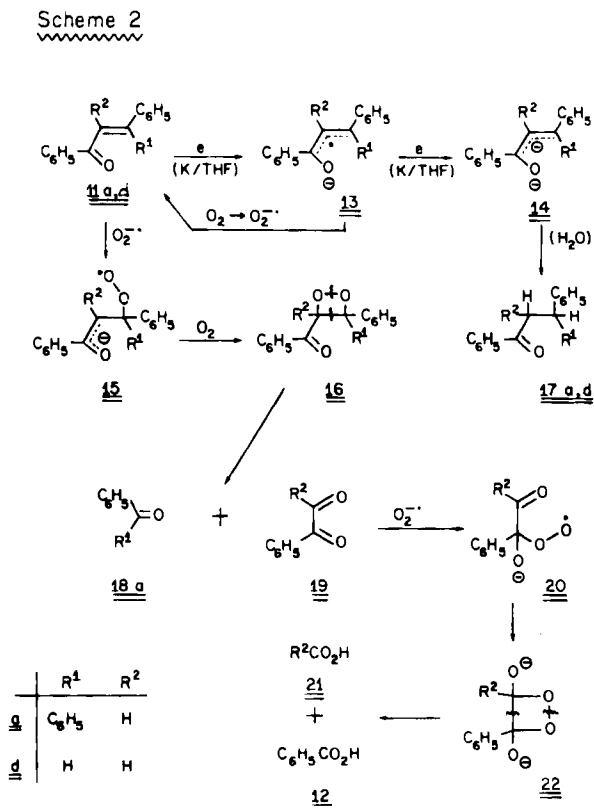


with oxygen, dissolved in the solvent or present as a contaminant under the reaction conditions, to give back the starting furanone and potassium superoxide. Mention may be made in this connection that several examples of superoxide formation by electron transfer to oxygen from radical anions and also electrochemical method are reported<sup>7</sup>. Subsequent reactions of superoxide with **1** could lead ultimately to the different products, as shown in Scheme 1.

Support for the involvement of superoxide in the transformations of **1 a–c** has been derived from the isolation of the same product mixture in the reaction of **1 a** with potassium superoxide. Thus, treatment of **1 a** with potassium superoxide in benzene containing 18-crown-6 gave a mixture of **7 a**, **11 a**, and **12**<sup>(6a)</sup>. Similarly, **1 c** yielded a mixture of **10 c**, **11 c**, and **12**<sup>(6b)</sup>.

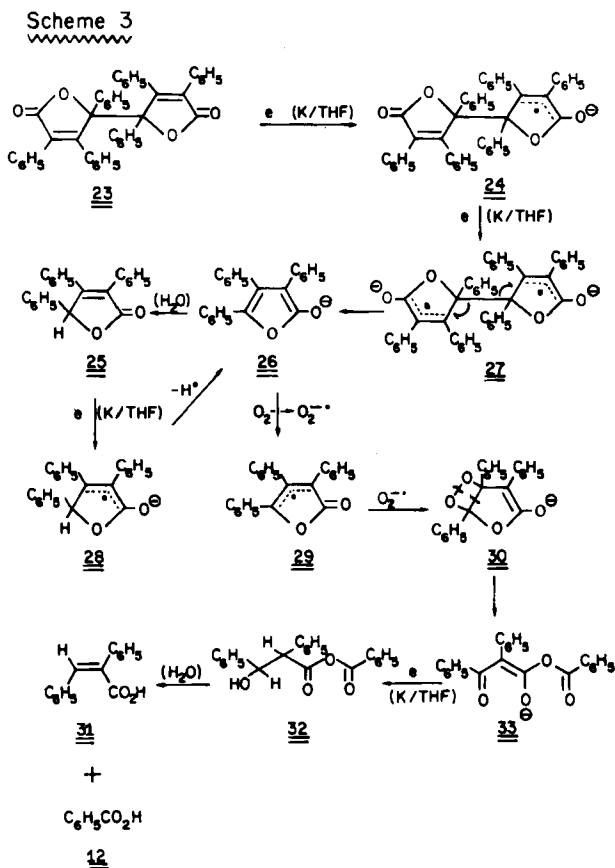
To examine whether the  $\alpha,\beta$ -unsaturated ketones (**11 a–c**), formed in the reaction of **1 a–c** with potassium, undergo further transformation leading to benzoic acid and other products, we have carried out the reactions of two representative examples such as **11 a** and 1,3-diphenyl-2-propen-1-one (**11 d**) with potassium. **11 a** gave a mixture of benzophenone (**18 a**),  $\beta,\beta$ -diphenylpropiophenone (**17 a**), and

benzoic acid (**12**)<sup>6a</sup>) (Scheme 2). When the reaction mixture was saturated with oxygen before workup, the same mixture consisting of **18a**, **17a**, and **12**<sup>6a</sup>) was obtained. Similarly, **11d** gave a mixture of  $\beta$ -phenylpropiophenone (**17d**) and **12**<sup>6a</sup>).



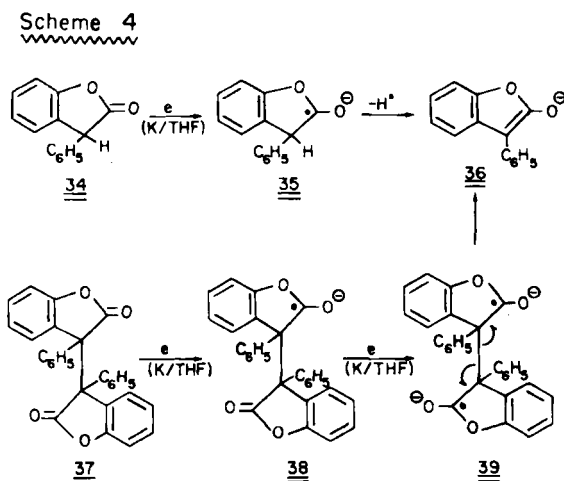
The formation of the different products in the reaction of **11a**–**d** with potassium could be understood in terms of the pathway shown in Scheme 2, involving radical anion (**13**) and dianion (**14**) intermediates, formed through electron transfer processes. The radical anion intermediate **13**, for example, can react with oxygen to give superoxide, which, in turn, subsequently interacts with the starting material (**11**) to give ultimately benzoic acid (**12**) (in the case of **11a**, **d**) and benzophenone (**18a**) (in the case of **11a**). The dianion intermediate **14**, on the other hand, can give rise to **17(a,d)**, on workup. In support of the assumption that products such as **18a** and **12** arise through the peroxide reaction of **11a** we have shown that treatment of **11a** with potassium superoxide in benzene containing 18-crown-6 gives a mixture of **18a** and **12**. It may be mentioned in this connection that *Rosenthal* and *Frimer*<sup>8)</sup> had observed earlier that potassium peroxide reacts with different  $\alpha,\beta$ -unsaturated ketones in aprotic solvents to give a mixture of carboxylic acids.

The reaction of a bifurandione such as **23** with potassium in THF gave a mixture of 3,4,5-triphenyl-2(5*H*)-furanone (**25**), 2,3-diphenylpropenoic acid (**31**), and benzoic acid (**12**)<sup>6b</sup> (Scheme 3). The same product mixture consisting of **25**, **31**, and **12** was obtained with excess potassium and longer reaction time. A probable pathway for the formation of the different products from **23** is shown in Scheme 3. It has been assumed that the bisradical anion intermediate **27**, formed through electron transfer reaction, fragments to the anionic species **26**, which on workup will give **25**. Further reaction of **25** with potassium will lead ultimately to **31** and



benzoic acid. In support of this assumption, the reaction of **25** with potassium in THF leads to a mixture of **31** and benzoic acid (**12**)<sup>6a</sup>. The same product mixture consisting of **31** and **12** was obtained when the reaction mixture was saturated with oxygen before workup. The formation of **31** and **12** from **25** through oxidation with superoxide, as indicated in Scheme 3, was supported by the observation that potassium superoxide oxidation of **25** in benzene containing 18-crown-6 gave the same mixture consisting of **31** and **12**<sup>6a</sup>.

In contrast to the reactions of **1a–c** and **25**, the reaction of 3-phenyl-2(3*H*)-benzofuranone (**34**) with potassium in THF did not give any isolable product; only the starting material (**34**) could be recovered unchanged. Similarly, when the reaction mixture was saturated with oxygen before workup, again only the starting material (**34**) could be recovered. The apparent inertness of **34** could be due to the formation of the anion **36**, which under the conditions of workup will give back the starting material (Scheme 4). It is interesting to note that the reaction of the bibenzofurandione **37** with potassium in THF, however, gave the benzofuranone **34** and it is likely that the bisradical anion **39** formed in this case may be fragmenting to **36**, which on workup will give **34** (Scheme 4).



### Cyclic Voltammetric Studies

To examine whether radical anion intermediates such as **2a–c**, **13**, **24**, **27**, **28**, **35**, **38**, and **39** are involved in the reaction of the different furanones and bifurandiones under investigation, an attempt was made to generate these intermediates electrochemically and to characterize them through their reaction potentials and electronic spectra. The values of the reduction peak potentials of the furanones (**1a–c**, **25**, **34**), bifurandiones (**23**, **37**), and  $\alpha,\beta$ -unsaturated ketones (**11a**, **d**) measured with respect to  $Ag/Ag^+$  reference electrode are given in Table 1. The cyclic voltammograms, A–F, of some representative compounds are shown in Fig. 1. Of these, compounds **1a**, **23**, **25**, **34**, and **37** exhibited irreversible peaks, while **11a** exhibited both a reversible and an irreversible peak. The single reduction peak observed in the case of **1a**, **b**, **c**, **25**, and **34** was between  $-2.26$  and  $-2.70$  V, which was attributed to the formation of the corresponding radical anions **2a–c**, **28**, and **35**, respectively. In the case of the bifurandiones **23** and **37**, however, two reduction peaks were observed corresponding to the radical anions **24** and **38**, respectively, and the bisradical anions **27** and **39**, respectively. Two reduction peaks were also observed for **11a** and **d** at potentials  $-1.96$ ,  $-2.4$  V and  $-1.78$ ,  $-2.4$  V, respectively. These peaks are attributed to the corresponding radical anions **13a**,

Table 1. Reduction potentials and spectral data of furanones, bifurandiones, and  $\alpha,\beta$ -unsaturated ketones

	Reduction potential ( $E_p$ ) <sup>a)</sup> V vs. Ag/Ag <sup>+</sup>	$\lambda_{\max}$ nm	Absorption maxima		Radical anion <sup>b,c)</sup> $10^{-3} \cdot \text{mol}^{-1} \text{cm}^{-1}$
			Starting material $10^{-3} \cdot \text{mol}^{-1} \text{cm}^{-1}$	$\epsilon_{\max}$ $\text{cm}^{-1}$	
<b>1a</b>	-2.70	270	21.7	290	36.6
				360	3.0
<b>1b</b>	-2.50	273	18.0	290	50.0
				390	1.5
<b>1c</b>	-2.48	279	14.0	285	18.5
				380	2.2
<b>25</b>	-2.26	279	20.0	420	23.8
<b>34</b>	-2.65	269	2.1	345	16.0
<b>23</b>	-1.25, -1.95	283	24.7	425	1.6
<b>37</b>	-1.65, -2.38	272	7.7	355	8.0
<b>11a</b>	-1.96, -2.40	300	12.5	345	8.35
<b>11d</b>	-1.78, -2.40	304	37.5	350	7.0

<sup>a)</sup> Reduction potential corresponding to the cathodic peak of the cyclic voltammogram. —

<sup>b)</sup>  $\pm 25\%$ . — <sup>c)</sup> Radical anions were stable under nitrogen during the recording of the spectra.

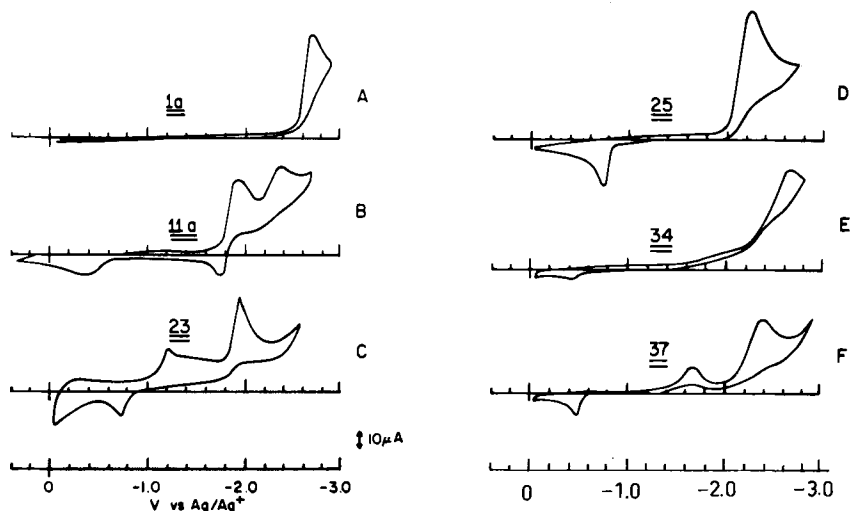


Fig. 1. Cyclic voltammograms of some representative compounds in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP). Sweep rate was 200 mV/s. Working electrode was a Pt microelectrode and reference electrode was Ag/Ag<sup>+</sup>

**d** and dianions **14a, d**, respectively. The first reduction of **11a** was reversible if the cathodic scan was reversed at  $-2.1$  V. If the scan is extended beyond  $-2.1$  V, then the radical anion gets converted to the dianion and under these circumstances the reversibility of the radical anion oxidation could not be observed, when the scan was reversed.

To characterize the radical anions generated from the furanones (**1a–c**, **25**, **34**), bifurandiones (**23**, **37**), and  $\alpha,\beta$ -unsaturated ketones (**11a**, **d**), we have electrochemically reduced these substrates in acetonitrile, in a specially designed cell, applying the requisite potentials and recording the absorption spectra. The spectral details, which are summarized in Table 1, indicate that the starting furanones and bifurandiones were characterized by an absorption maximum around 260–283 nm, whereas the  $\alpha,\beta$ -unsaturated ketones **11a**, **d** showed an absorption maximum around 300–304 nm. The corresponding radical anions exhibited a red-shifted absorption maximum around 345–425 nm; the radical anions of **1a–c** exhibited an additional absorption band around 285–290 nm.

Since the reduction peak potentials of the furanones, bifurandiones, and  $\alpha,\beta$ -unsaturated ketones under investigation are greater than the reduction potential of oxygen ( $E_p = -0.90$  V vs. SCE)<sup>7d</sup>, one would expect quenching of the radical anions, derived from these substrates, by oxygen. Indeed, all the radical anions from **1a–c**, **25**, **34**, **23**, **37**, **11a** and **d** were quenched by oxygen, as evidenced by the disappearance of their absorption bands, on bubbling oxygen through their solutions in acetonitrile. It is quite likely that these radical anions react with oxygen to give superoxide, as implicated in Schemes 1–3. The quenching of **35** with oxygen, however, resulted in the generation of the starting material (**34**) (Scheme 4).

## Conclusions

Radical anion and dianion intermediates are formed through electron transfer process in the reaction of furanones and bifurandiones with potassium in THF. These reactive intermediates were also formed under electrochemical reduction of the appropriate substrates and were characterized by red-shifted absorption maxima in their electronic spectra. They were quenched by oxygen to give several oxygenated and fragmentation products. Reasonable mechanisms have been suggested to account for the formation of the different products. Some of the oxygenation products were also observed in the oxidation of representative furanones and bifurandiones with potassium superoxide, thereby supporting the suggested pathways.

We thank the *Department of Science and Technology, Government of India, Indian Institute of Technology, Kanpur*, and the *Office of Basic Energy Sciences of the U. S. Department of Energy* for financial support of this work.

## Experimental Part

Melting points: uncorrected, Mel-Temp melting point apparatus. — IR spectra: Perkin Elmer Model 377 or 580 infrared spectrophotometers. — Electronic spectra: Cary 219 or Beckman DB spectrophotometers. — NMR spectra: Varian EM-390 NMR spectrometer, tetramethylsilane internal standard. — Mass spectra: Varian MAT CH7, 70 eV. — Petroleum ether used was the fraction with b. p. 60–80°C. THF was dried over sodium and was distilled immediately before use. Gold Label (Aldrich) acetonitrile was used for cyclic voltammetric studies.



**Starting Materials:** 3,3,5-Triphenyl-2(3*H*)-furanone (**1a**)<sup>9</sup>, m. p. 121 °C, 3-methyl-3,4,5-triphenyl-2(3*H*)-furanone (**1b**)<sup>10</sup>, m. p. 118–119 °C, 3,3,4,5-tetraphenyl-2(3*H*)-furanone (**1c**)<sup>11</sup>, m. p. 137 °C, 1,3,3-triphenyl-2-propen-1-one (**11a**)<sup>9</sup>, m. p. 92–93 °C, 1,3-diphenyl-2-propen-1-one (**11d**)<sup>12</sup>, m. p. 56–57 °C, 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5'(2*H*,2'*H*)-dione (**23**)<sup>10</sup>, m. p. 273–274 °C, 3,4,5-triphenyl-2(5*H*)-furanone (**25**)<sup>13</sup>, m. p. 124–125 °C, 3-phenyl-2(3*H*)-benzofuranone (**34**)<sup>14</sup>, m. p. 113–114 °C, and 3,3'-diphenyl-3,3'-bibenzofuran-2,2'(3*H*,3'*H*)-dione (**37**)<sup>15</sup>, m. p. 175–176 °C, were prepared by reported procedures.

**Reaction of 2(3*H*)-Furanones 1a–c with Potassium in THF:** A general procedure was to shake a mixture of 5.0 mmol of the appropriate furanone with potassium (10 mmol) in THF (125 ml) in a Schlenk tube for several h. A few clean, broken glass pieces were added to the mixture to ensure a fresh surface of the metal throughout the reaction. The reaction mixture invariably underwent pronounced color changes, indicative of the formation of radical anion intermediates. On completion of the reaction, the mixture was poured into moist THF (100 ml) to destroy any unchanged potassium and the solvent was removed under vacuum. The residual solid was treated with 10 ml of water and extracted with methylene chloride (100 ml). Workup of the methylene chloride extract by removal of the solvent under vacuum and fractional crystallization or chromatography over silica gel, followed by crystallization gave the non-acidic products. Acidification of the aqueous layer with dilute hydrochloric acid and extraction with methylene chloride (100 ml) gave the carboxylic acid fraction, which was recrystallized.

**Reaction of 1a:** Treatment of **1a** (1.56 g, 5.0 mmol) with potassium (400 mg, 10 mmol) in THF for 10 h and workup in the usual manner gave 240 mg (39%) of **12**, m. p. 121–122 °C (mixture m. p.), 350 mg (22%) of **1a** (chromatography over silica gel and elution with benzene/petroleum ether (1:9), followed by recrystallization from methanol), m. p. 121 °C (mixture m. p.), 220 mg (14%) of **11a**<sup>9</sup> (elution of the silica gel column with benzene/petroleum ether (1:4), followed by recrystallization from the same solvent mixture), m. p. 92 °C (mixture m. p.), and 285 mg (17%) of **7a** (elution with ethyl acetate/benzene (1:9), followed by recrystallization from benzene/petroleum ether (1:3)), m. p. 180 °C (mixture m. p.).

On treatment of **1a** (5.0 mmol) with potassium (10 mmol) for 20 h, the corresponding yields of **12**, recovered **1a**, **11a**, and **7a** were 57, 14, 13, and 11%, respectively. Treatment of **1a** (5.0 mmol) with potassium (10 mmol) for 10 h, followed by saturating the reaction mixture with oxygen for 20 min gave **12**, **1a** (recovered), **11a**, and **7a** in 51, 24, 14, and 12% yields, respectively. Treatment of **1a** (5.0 mmol) with potassium (10 mmol) in oxygen saturated THF (125 ml) for 10 h gave **12**, **1a** (recovered), **11a**, and **7a** in 18, 24, 8, and 19%, respectively.

**Reaction of 1b:** Treatment of **1b** (820 mg, 2.5 mmol) with potassium (200 mg, 5.0 mmol) for 5 h gave 260 mg (30%) of **7b**<sup>10</sup>, m. p. 174–175 °C (mixture m. p., recrystallized from benzene/petroleum ether), 75 mg (9%) of **1b**<sup>10</sup>, m. p. 118–119 °C (mixture m. p.), and 80 mg (11%) of **11b**<sup>16</sup>, m. p. 100–101 °C (mixture m. p.) (recrystallization from benzene/petroleum ether (1:4)).

On treatment of **1b** (2.5 mmol) with potassium (5.0 mmol) for 5 h, followed by saturation of the reaction mixture with oxygen for 20 min gave 15 mg (5%) of **12**, m. p. 120–121 °C (mixture m. p.), along with **1b** (9%), **7b** (29%) and **11b** (9%).

**Reaction of 1c:** Treatment of **1c** (970 mg, 2.5 mmol) with potassium (200 mg, 5.0 mmol) for 10 h and workup in the usual manner gave 230 mg (38%) of **12**, m. p. 120–121 °C (mixture m. p.), 80 mg (9%) of **11c**<sup>17</sup>, m. p. 152–153 °C (mixture m. p., recrystallized from benzene/petroleum ether (9:1)), and 300 mg (30%) of **10c**, m. p. 178–179 °C (recrystallization from benzene/petroleum ether): IR (KBr): 3300 (OH), 3100, 3065, and 3030 (CH),

1755 (C=O), 1600 (C=C)  $\text{cm}^{-1}$ . — UV (methanol):  $\lambda_{\text{max}}$  240 nm ( $\epsilon$  22330), 280 (365). —  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 4.0 (1H, s, OH,  $\text{D}_2\text{O}$ -exchangeable), 4.6 (1H, s, methine), 6.6 (20H, m, aromatic). — MS:  $m/z$  (relative intensity, %): 406 ( $\text{M}^+$ , 20), 388 ( $\text{M}^+ - \text{H}_2\text{O}$ , 26), 360 ( $\text{M}^+ - \text{H}_2\text{O}$ ,  $-\text{CO}$ , 19), and other peaks.

$\text{C}_{28}\text{H}_{22}\text{O}_3$  (406.5) Calcd. C 82.75 H 5.21 Found C 83.25 H 5.29

*Acid-catalyzed Conversion of 10c to 1c:* Dry HCl gas was passed through a solution of **10c** (200 mg, 0.50 mmol) in THF (10 ml) for 10 min. Removal of the solvent under vacuum gave a solid, which was extracted with methylene chloride. The extract was washed with water, dried over sodium sulfate, and the solvent was removed under vacuum to give 165 mg (82%) of **1c**, m. p. 136–137°C (mixture m. p.), after recrystallization from benzene and petroleum ether (1:2).

*Reaction of  $\alpha,\beta$ -Unsaturated Carbonyl Compounds 11a and d with Potassium in THF:* The experimental procedure was similar to that employed in the case of 2(3H)-furanones (**1a–c**).

*Reaction of 11a:* Treatment of 1.42 g (5.0 mmol) of **11a** with potassium (400 mg, 10 mmol) in THF (125 ml) for 10 h gave 50 mg (8%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.), 60 mg (7%) of benzophenone (**18a**), m. p. 49–50°C (mixture m. p.) (elution with petroleum ether from a silica gel column, followed by recrystallization from the same solvent), 712 mg (50%) of **17a**<sup>18</sup>, m. p. 92°C (mixture m. p.) (elution with benzene/petroleum ether (1:9) from the silica gel column), and 430 mg (30%) of **11a**, m. p. 92°C (mixture m. p.).

On treatment of **11a** (5.0 mmol) with potassium (10 mmol) for 10 h and saturation of the reaction mixture with oxygen for 20 min before workup, the corresponding yields of **12**, **18a**, **17a**, and **11a** were 10, 8, 49, and 28%, respectively.

*Reaction of 11d:* Treatment of 2.08 g (10 mmol) of **11d** with potassium (780 mg, 20 mmol) for 15 h gave 230 mg (19%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.) and 600 mg (29%) of **17d**<sup>19</sup>, m. p. 69–70°C (mixture m. p.).

*Reaction of 23 with Potassium in THF:* A mixture of **23** (620 mg, 1.0 mmol) and potassium (70 mg, 2.0 mmol) was shaken in THF (125 ml) for 4 h, the reaction mixture becoming yellow at first and later turning brown. Workup as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum gave a solid, which was treated with water (5 ml). Extraction with methylene chloride gave a product mixture, which was chromatographed over silica gel. Elution with benzene/petroleum ether (1:4) gave 220 mg (35%) of **25**, m. p. 124–125°C (mixture m. p., recrystallized from methanol). Further elution with benzene/petroleum ether (1:1) gave 127 mg (26%) of **31**, m. p. 170–171°C (mixture m. p., recrystallized from ethanol). The aqueous layer (after extraction with methylene chloride) was acidified with dilute hydrochloric acid and extracted with benzene to give 50 mg (20%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.).

On treatment of **23** (1.0 mmol) with excess potassium (4.0 mmol) in THF (125 ml) for 6 h, the corresponding yields of **25**, **31**, and **12** were 32, 29, and 22%, respectively.

*Reaction of 25 with Potassium in THF:* Treatment of 1.56 g (5.0 mmol) of **25** with potassium (400 mg, 10 mmol) in THF (125 ml) for 10 h and workup as in the case of **23** gave 130 mg (8%) of **25**, m. p. 124–125°C (mixture m. p.), 890 mg (74%) of **31**, m. p. 171°C (mixture m. p.), and 110 mg (18%) of **12**, m. p. 120–121°C (mixture m. p.).

On treatment of **25** (5.0 mmol) with potassium (10 mmol) for 10 h and saturation of the reaction mixture with oxygen for 20 min before workup, the yields of **25**, **31**, and **12** were 8, 79, and 21%, respectively.

*Reaction of 34 with Potassium in THF:* Treatment of 1.05 g (5.0 mmol) of **34** with potassium (400 mg, 10 mmol) in THF (125 ml) for 24 h and workup as in the earlier cases gave 700 mg

(67%) of the starting material (**34**), m. p. 113–114°C. In a repeat experiment, **34** (5.0 mmol) was treated with excess potassium (20 mmol) for 24 h. Workup in the usual manner gave 58% of **34**, m. p. 113–114°C (mixture m. p.). On treatment of **34** (5.0 mmol) with potassium (10 mmol) for 24 h and saturating the reaction mixture with oxygen before workup, the corresponding recovery of **34** was 57%.

*Reaction of 37 with Potassium in THF:* Treatment of 500 mg (1.2 mmol) of **37** with potassium (100 mg, 2.5 mmol) in THF (125 ml) for 10 h and workup as in the earlier cases gave 290 mg (58%) of **34**, m. p. 113–114°C (mixture m. p.). On treatment of **37** (1.2 mmol) with excess of potassium (5.0 mmol) for 10 h, the corresponding yield of **34** was 55%.

*Reaction of 1a, c and 11c with Potassium Superoxide:* A general procedure was to stir an equimolar mixture of the starting material, potassium superoxide, and 18-crown-6 in benzene (100 ml) for 20–30 h at room temp., protected from light. The mixture was poured into water (20 ml) and extracted several times with small portions of aqueous sodium chloride. The aqueous fractions were combined, acidified with dilute hydrochloric acid, extracted with benzene to give the carboxylic acids, which were further purified by recrystallization. The benzene fractions (after removal of the aqueous layer from the initial reaction mixture) was worked up by chromatography or fractional crystallization to give the non-acidic products.

*Reaction of 1a:* Treatment of 936 mg (6.0 mmol) of **1a** with 485 mg (3.0 mmol) of potassium superoxide and 795 mg (3.0 mmol) of 18-crown-6 for 24 h and workup in the usual manner gave 120 mg (13%) of the starting material (**1a**), 70 mg (19%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.), 80 mg (9%) of **11a**, m. p. 92°C (mixture m. p.), and 600 mg (61%) of **7a**, m. p. 180–181°C (mixture m. p.).

*Reaction of 1c:* Stirring a mixture of 485 mg (1.25 mmol) of **1c**, 180 mg (2.5 mmol) of potassium superoxide, and 325 mg (1.25 mmol) of 18-crown-6 in benzene for 24 h and workup in the usual manner gave 75 mg (49%) of **12**, m. p. 120–121°C (mixture m. p.), 65 mg (13%) of the starting material (**1c**), 30 mg (7%) of **11c**, m. p. 152–153°C (mixture m. p.), and 280 mg (55%) of **10c**, m. p. 178–179°C (mixture m. p.).

*Reaction of 11a:* Treatment of 296 mg (1.0 mmol) of **11a** with 144 mg (2.0 mmol) of potassium superoxide and 265 mg (1.0 mmol) of 18-crown-6 for 30 h and workup in the usual manner gave 75 mg (31%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.), 120 mg (41%) of the starting material (**11a**), and 70 mg (38%) of benzophenone (**18a**), m. p. 49–50°C (mixture m. p.).

*Reaction of 25 with Potassium Superoxide:* Stirring a mixture of 780 mg (2.5 mmol) of **25**, 360 mg (5.0 mmol) of potassium superoxide, and 660 mg (2.5 mmol) of 18-crown-6 in benzene (100 ml) for 24 h and workup as in the earlier cases gave 300 mg (49%) of benzoic acid (**12**), m. p. 120–121°C (mixture m. p.), and 455 mg (76%) of **31**, m. p. 171–172°C (mixture m. p.).

*Cyclic Voltammetry:* Measurements were made with a Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat, a PAR Model 175 Universal Programmer, and a Kipp and Zonen X–Y recorder. Experiments were performed in a standard three compartment cell equipped with a Pt-disc working electrode, Pt-wire counter electrode, and Ag/Ag<sup>+</sup> reference electrode. The cyclic voltammograms were recorded in acetonitrile with 0.2 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The direction of the initial scan was cathodic and the scan rate was 200 mV/s. For spectroelectrochemical measurements, a specially designed cell was employed which consists of an extended 10 mm quartz cuvette, equipped with a Pt-gauze working electrode, a Pt-foil counter electrode, and a Ag/Ag<sup>+</sup> reference electrode. The electrolysis experiments were carried out in acetonitrile solu-

tions ( $\approx 0.05$  mm) under nitrogen at controlled potentials, and the absorption spectra of the electrochemically generated radical anions were recorded directly in a Cary 219 spectrophotometer. Electron reduction processes were monitored directly using a PAR 179 Digital Coulometer.

#### CAS-Registry Numbers

**1a:** 2313-03-3 / **1b:** 31589-99-8 / **1c:** 6963-25-3 / **7a:** 90267-02-0 / **7b:** 31554-22-0 / **10c:** 99765-21-6 / **11a:** 849-01-4 / **11b:** 25118-77-8 / **11c:** 6333-11-5 / **11d:** 94-41-7 / **12:** 65850 / **17a:** 606-86-0 / **17d:** 1083-30-3 / **18a:** 119619 / **23:** 31554-23-1 / **25:** 7404-46-8 / **31:** 3368-16-9 / **34:** 3117-37-1 / **37:** 65425-10-7 / **K:** 7440-09-7 / **O<sub>2</sub>:** 7782-44-7 / **KO<sub>2</sub>:** 12030-88-5

<sup>1)</sup> Document No. NDRL-2677 from the Notre Dame Radiation Laboratory.

<sup>2a)</sup> Indian Institute of Technology. — <sup>2b)</sup> University of Notre Dame.

<sup>3)</sup> For a review on the addition of alkali metals to unsaturated systems, see V. Kalyanaraman and M. V. George, *J. Organomet. Chem.* **47**, 225 (1973).

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<sup>6a)</sup> Yield based on the assumption that one mol of benzoic acid is formed. — <sup>6b)</sup> Yield based on the assumption that two mol of benzoic acid are formed.

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