

## Formation and Reactions of 1-Phenyl-2-propanone Dianion and Related Systems with Electrophilic Reagents<sup>1</sup>

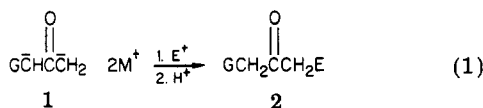
G. B. Trimitsis,<sup>\*2a</sup> J. M. Hinkley,<sup>2b</sup> R. TenBrink,<sup>2b</sup> A. L. Faburada,<sup>2b</sup> R. Anderson,<sup>2a</sup> M. Poli,<sup>2b</sup> B. Christian,<sup>2a</sup> G. Gustafson,<sup>2b</sup> J. Erdman,<sup>2b</sup> and D. Rop<sup>2b</sup>

Departments of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, and University of Pittsburgh at Johnstown, Johnstown, Pennsylvania, 15904

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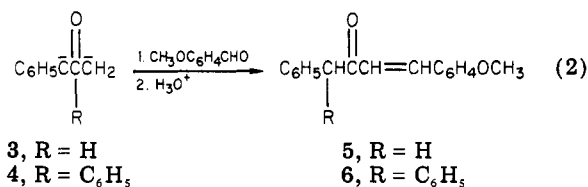
1-Phenyl-2-propanone, 1,1-diphenyl-2-propanone, and 1-(4-methoxyphenyl)-2-propanone were converted to their dicarbanions **3**, **4**, and **31**, respectively, and their reactions with a number of electrophilic reagents were examined. All three dianions gave a mixture of C-1 and C-3 alkylation products when treated with alkyl halides of higher reactivity, while only C-1 alkylations occurred when alkyl halides of lower reactivity were used. It was also found that the 1,1-diphenyl-2-propanone and the 1-(4-methoxyphenyl)-2-propanone dianions **4** and **31** gave a higher ratio of C-1/C-3 alkylation products than the 1-phenyl-2-propanone dianion **3**. When dianion **3** was reacted with *p*-anisaldehyde and a number of protonating agents, electrophilic attack occurred exclusively at the C-3 position. The trends observed are analyzed, and mechanisms are proposed to account for the results obtained.

Literature reports during the past quarter century have amply demonstrated that dicarbanions of the general formula **1** react with a variety of electrophilic reagents to give products of structure **2** (eq 1), resulting from *exclusive*



attack at the site of secondary ionization, i.e., the terminal methylene position.<sup>3</sup> These results have been explained by arguing that the site of secondary ionization (C<sub>2</sub>) bears a higher electron density than the site of primary ionization (C<sub>1</sub>) and that therefore it should be more nucleophilic.<sup>3,4</sup>

Two systems reported to follow the general pattern of reactivity described above were the dicarbanions **3** and **4** of 1-phenyl-2-propanone and 1,1-diphenyl-2-propanone, respectively.<sup>3j</sup> Thus, upon treatment of intermediates **3** and **4** with *p*-anisaldehyde, the terminal condensation products **5** and **6** were obtained (eq 2).



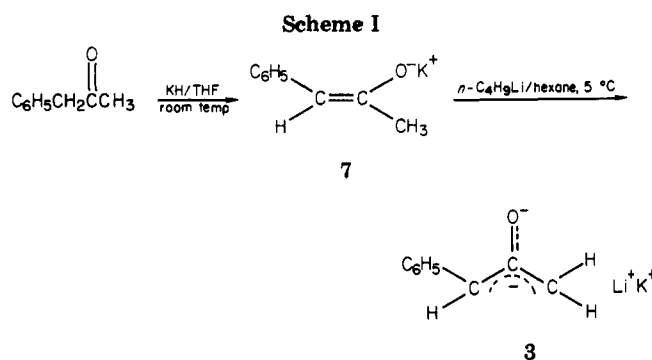
Contrary to these results, recent work in the authors' laboratory showed that unlike other dicarbanions, inter-

(1) Part of this work appeared as a preliminary communication: Trimitsis, G. B.; Hinkley, J. M.; TenBrink, R.; Poli, M.; Gustafson, G.; Erdman, J.; Rop, D. *J. Am. Chem. Soc.* 1977, 99, 4838. For a study involving the methylation of the 1-phenyl-2-propanone dianion, which appeared subsequent to our preliminary communication, see: Bays, J. P. *J. Org. Chem.* 1978, 43, 38.

(2) (a) University of Pittsburgh at Johnstown. (b) Western Michigan University.

(3) (a) Kaiser, E. M.; Petty, J. D.; Knutson, P. L. *A. Synthesis*, 1977, 509. (b) Bhanu, S.; Scheinmann, F. *J. Chem. Soc., Chem. Commun.* 1975, 817. (c) McMurry, J. E.; Musser, J. H. *J. Org. Chem.* 1975, 40, 2556. (d) Sancaktar, E. A.; Taylor, J. D.; Hay, J. V.; Wolfe, J. F. *Ibid.* 1976, 41, 509. (e) Depres, J. P.; Greene, A. E.; Crabbe, *Tetrahedron Lett.* 1978, 2191. (f) Grieco, P. A.; Pogonowski, C. S. *J. Am. Chem. Soc.* 1973, 95, 3071. (g) Huckin, S. N.; Weiler, L. *Ibid.* 1974, 96, 1082. (h) O'Sullivan, W. I.; Travares, D. F.; Hauser, C. R. *Ibid.* 1961, 83, 3453. (i) Hauser, C. R.; Harris, T. M. *Ibid.* 1958, 80, 6360. (j) Mao, C. L.; Hauser, C. R.; Miles, M. L. *Ibid.* 1967, 89, 5303. (k) Sandifer, R. M.; Bhattacharya, A. K.; Harris, T. M. *J. Org. Chem.* 1981, 46, 2260.

(4) For a discussion involving chemical reactivity as a function of charge density, see: Dewar, M. J. S. *Adv. Chem. Phys.* 1965, 8, 102.



mediates **3** and **4** react with alkyl halides to give products resulting from electrophilic attack at the methine rather than the methylene site.

This paper describes the reactions of dicarbanions **3** and **4** and certain related systems with a variety of alkyl halides and proton donors and analyzes the trends observed. In addition, mechanisms are proposed to account for the observed results.

## Results

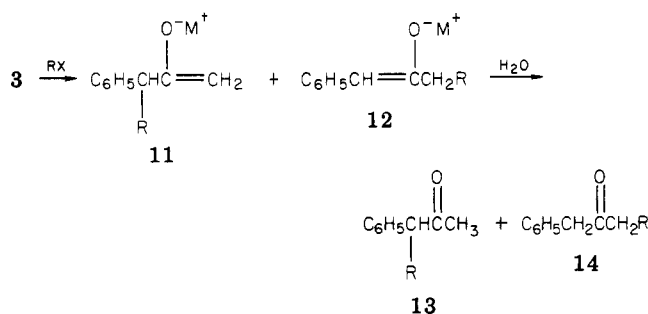
The 1-phenyl-2-propanone dianion **3** was initially generated by Hauser and his co-workers through sequential treatment of the parent ketone with an alkali amide in liquid ammonia followed by reaction of the resulting enolate monoanion with *n*-butyllithium in tetrahydrofuran (THF)-hexane.<sup>3j</sup> In our laboratories, a more convenient method was developed for the formation of dianion **3**, involving initial treatment of the parent ketone with potassium hydride in THF, followed by *n*-butyllithium (Scheme I).

In view of the unusual reactions of dianion **3** described herein, it became necessary to document clearly the sequence of reactions leading to its formation (Scheme I). The presence of enolate **7** was ascertained by treatment of the KH-generated intermediate with iodomethane to produce the expected C<sub>1</sub> alkylation product, 3-phenyl-2-butanone (**8**), in good yield (see Experimental Section for details). Enolate **7** was considered to possess the *trans* rather than the *cis* geometry on the basis of its <sup>1</sup>H NMR spectrum, recorded in THF; the latter displayed, in addition to the aromatic absorptions, a sharp singlet at δ 4.5 for the proton at C<sub>1</sub>. The *cis* isomer has been shown to display a <sup>1</sup>H NMR absorption for H<sub>1</sub> at a considerably lower field.<sup>5</sup>

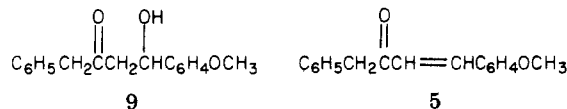
Table I. Alkylations of 1-Phenyl-2-propanone Dianion 3

| alkyl halide            | C <sub>1</sub> product                  | C <sub>3</sub> product      | C <sub>1</sub> /C <sub>3</sub> ratio | overall % yield |
|-------------------------|---|-----------------------------|--------------------------------------|-----------------|
| iodomethane             | 3-phenyl-2-butanone (8)                 | 1-phenyl-2-butanone (15)    | 1.2:1                                | 62              |
| iodoethane              | 3-phenyl-2-pentanone (16)               | 1-phenyl-2-pentanone (17)   | 5:1                                  | 65              |
| 1-chloropropene         | 3-phenyl-5-hexen-2-one (18)             | 1-phenyl-5-hexen-2-one (19) | 8:1                                  | 66              |
| 1-iodobutane            | 3-phenyl-2-heptanone (20)               | 1-phenyl-2-heptanone (21)   | 9:1                                  | 57              |
| 1-chlorobutane          | 3-phenyl-2-heptanone (22)               |                             | only C <sub>1</sub>                  | 70              |
| 1-bromo-2-methylpropane | 5-methyl-3-phenyl-2-hexanone (23)       |                             | only C <sub>1</sub>                  | 72              |
| 2-bromopropane          | 4-methyl-3-phenyl-2-pentanone (24)      |                             | only C <sub>1</sub>                  | 63              |
| 2-bromobutane           | 4-methyl-3-phenyl-2-hexanone (25)       |                             | only C <sub>1</sub>                  | 63              |
| bromomethylcyclohexane  | 4-cyclohexyl-3-phenyl-2-butanone (26)   |                             | only C <sub>1</sub>                  | 73              |
| α-chlorotoluene         | 3,4-diphenyl-2-butanone (27)            |                             | only C <sub>1</sub>                  | 52              |
| bromocyclopentane       | 1-cyclopentyl-1-phenyl-2-propanone (28) |                             | only C <sub>1</sub>                  | 62              |
| bromocyclohexane        | 1-cyclohexyl-1-phenyl-2-propanone (29)  |                             | only C <sub>1</sub>                  | 61              |

Scheme II



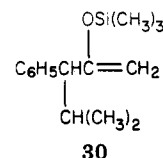
The presence of dianion 3 was confirmed in two ways. First, dianion 3 was reacted with 1 equiv of *p*-anisaldehyde to produce the terminal aldol condensation product 9, in 44% yield, which upon dehydration gave the corresponding α,β-unsaturated ketone 5, previously reported by Hauser.<sup>3j</sup>



Second, dianion 3, was generated in THF-*d*<sub>6</sub>-hexane, and its <sup>1</sup>H NMR spectrum was recorded by using a 60-MHz instrument and tetramethylsilane (Me<sub>4</sub>Si) as an external standard. The absorptions displayed in the NMR spectrum of 3 and their corresponding assignments were as follows: broad multiplet at δ 6.33 (4 H), assigned to the ortho and meta protons of the benzene ring; broad multiplet at δ 5.47 (1 H), assigned to the para proton; broad singlet at δ 3.82 (1 H), assigned to the proton at C<sub>1</sub>; partially resolved doublet centered at δ 2.60 (2 H), assigned to the protons at C<sub>3</sub>.

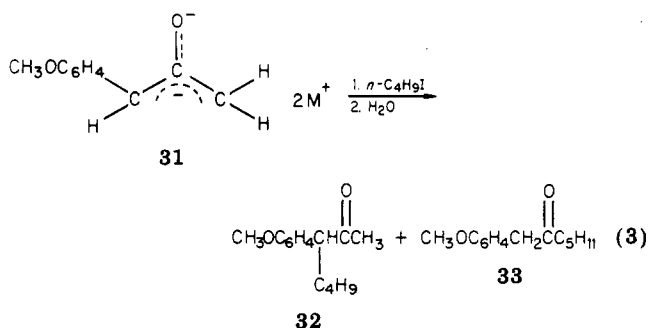
Dianion 3 was reacted with a variety of primary, secondary, and allylic alkyl halides to afford varying amounts of C<sub>1</sub> and C<sub>3</sub> alkylation products 13 and 14, respectively, depending upon the nature of the halide used (see Scheme II and Table I). Thus, all of the secondary alkyl halides used, i.e., 2-bromopropane, 2-bromobutane, bromocyclopentane, and bromocyclohexane, as well as the primary alkyl halides 1-bromo-2-methylpropane, (bromomethyl)cyclohexane, and 1-chlorobutane, afforded C<sub>1</sub> alkylation products exclusively (Table I). Reaction of dianion 3 with more reactive primary alkyl halides, on the other hand, gave C<sub>1</sub> and C<sub>3</sub> alkylation products ranging from a ca. 1:1 mixture in the case of iodomethane to a 9:1 mixture in favor of the C<sub>1</sub> product in the case of 1-iodobutane.

Finally, when dianion 3 was treated sequentially with 1.2 equiv of 2-bromopropane and 1.5 equiv of trimethylchlorosilane, the C<sub>1</sub>-alkylated silylenol ether 30 was obtained in 78% yield.



In addition to the alkylations of dianion 3, its protonation by means of water, deuterium oxide, methanol, ethanol, and ammonium chloride was also examined. Dianion 3 was carefully titrated with 1 equiv of the protonating agent in THF-hexane, and the <sup>1</sup>H NMR of the resulting reaction mixture was recorded by using a 60-MHz spectrometer and Me<sub>4</sub>Si as an external standard. The disappearance of the intensely red color of the dianion was used as an indicator. In all cases, the NMR spectrum of the reaction mixture was found to be identical with that of the enolate monoanion 7 (Scheme I) described earlier. These results strongly suggest that, while alkylations of the 1-phenyl-2-propanone dianion 3 occur predominantly at the methine site, protonation occurs exclusively at the terminal methylene position.

Next, 1-(4-methoxyphenyl)-2-propanone was converted to its dianion 31, and the alkylation of the latter with 1-iodobutane was investigated. Dianion 31 was generated by the potassium hydride-*n*-butyllithium method described earlier. Reaction of 31 with 1-iodobutane afforded a mixture of C<sub>1</sub> and C<sub>3</sub> alkylation products 32 and 33 (eq 3) in a ratio of 1.9:1.0, and an overall yield of 73%.



Finally, 1,1-diphenyl-2-propanone was also converted to its dianion 4 by means of potassium hydride and *n*-butyllithium, and the reactions of the latter with several alkyl halides were studied. The results are shown in Table II. It can be seen that secondary alkyl halides afforded predominantly C<sub>1</sub> alkylation products, while alkylation using primary halides gave primarily C<sub>3</sub> products.

(5) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* 1973, 38, 514.

Table II. Alkylations of 1,1-Diphenyl-2-propanone Dianion 4

| alkyl halide    | C <sub>1</sub> product                 | C <sub>3</sub> product                 | C <sub>1</sub> /C <sub>3</sub> ratio | overall % yield |
|-----------------|--|--|--------------------------------------|-----------------|
| iodomethane     | 3,3-diphenyl-2-butanone (34)           | 1,1-diphenyl-2-butanone (35)           | 1.1:1.0                              | 77              |
| bromoethane     | 3,3-diphenyl-2-pentanone (36)          | 1,1-diphenyl-2-pentanone (37)          | 1.0:1.6                              | 87              |
| 1-chloropropane | 3,3-diphenyl-2-hexanone (38)           | 1,1-diphenyl-2-hexanone (39)           | 1.0:1.2                              | 87              |
| 2-bromopropane  | 3,3-diphenyl-4-methyl-2-pentanone (40) | 1,1-diphenyl-4-methyl-2-pentanone (41) | 1.8:1.0                              | 54              |
| 2-chloropropane | 3,3-diphenyl-4-methyl-2-pentanone (40) | 1,1-diphenyl-4-methyl-2-pentanone (41) | 4.3:1.0                              | 60              |

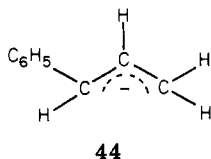
### Discussion

The results described in the previous section clearly indicate that in their alkylation reactions dianions 3, 4, and 31 deviate markedly from the traditionally held view that such intermediates react with electrophilic reagents essentially exclusively at the site of secondary ionization. Instead, it was observed that in all cases either alkylations occurred exclusively at the site of *primary* ionization or mixtures of products were obtained as a result of electrophilic attack at both the primary and secondary carbanionic sites.

To ascertain that alkylation at C<sub>1</sub> did indeed occur through the dianion intermediate 3 to give the enolate monoanion 11 as shown in Scheme II, an experiment was performed where dianion 3 was sequentially treated with ca. 1 equiv each of 2-bromopropane and trimethylchlorosilane. The reaction afforded the silyl enol ether 30 containing an isopropyl group at the C<sub>1</sub> position.

By examining the experimental results, it can be seen that the specific course of the alkylation reactions depended substantially on the reactivity of the alkyl halide used. For example, reaction of the 1-phenyl-2-propanone dianion 3 with the less reactive secondary alkyl halides afforded essentially exclusively C<sub>1</sub> alkylation products, while reaction of dianion 3 with a number of primary alkyl halides and one allylic halides gave mixtures of C<sub>1</sub> and C<sub>3</sub> alkylation products (Table I).

A suitable explanation for the alkylation pattern of the 1-phenyl-2-propanone dianion 3 can be offered by taking into account the overall charge distribution in this intermediate as revealed by its <sup>1</sup>H NMR spectrum. Thus, the overall appearance of the spectrum of dianion 3 is remarkably similar to that of the allylbenzene anion 44, reported earlier by Freedman and his co-workers.<sup>6</sup> The close resemblance of their NMR spectra strongly implies a close structural similarity between the two carbanion intermediates. Indeed, if one of the negative charges in dianion 3 is considered to be largely localized on the oxygen,<sup>7</sup> the lower portion of this intermediate would constitute a system essentially identical with the allylbenzene anion 44, with the second negative charge highly delocalized over C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and the benzene ring.



An observation of interest in connection with the NMR spectra of the two intermediates 3 and 44 is that, at comparable temperatures, the spectrum of dianion 3 displayed

less sharply defined absorptions than the allylbenzene anion 44, indicating that the barrier of rotation around the C<sub>6</sub>H<sub>5</sub>-C<sub>1</sub>, C<sub>1</sub>-C<sub>2</sub>, and C<sub>2</sub>-C<sub>3</sub> bonds in the former intermediate is lower than in the latter.

The mode of alkylation of the 1-phenyl-2-propanone dianion 3 closely parallels that described in the literature for the allylbenzene anion 44. Thus, numerous studies<sup>8</sup> have shown that alkylations of carbanion 44 under a variety of experimental conditions occurred largely at the carbon adjacent to the benzene ring (C<sub>1</sub> alkylation). Terminal alkylation products were also formed during these reactions, but in smaller quantities.<sup>8b,c</sup> It was further shown that the amount of terminal alkylation products formed was largely dependent upon the reactivity of the alkyl halide used, the more reactive halides producing larger quantities of terminal alkylation products.

The close similarity in the alkylation patterns of dianion 3 and the allylbenzene anion 44 is very much in line with the close structural similarity of these two intermediates suggested earlier on the basis of their NMR spectra. The higher reactivity of the carbon atom adjacent to the benzene ring in both intermediates can be best explained by recognizing that the presence of the benzene ring will cause the accumulation of a higher electron density on C<sub>1</sub> relative to C<sub>3</sub>.<sup>8d,9-11</sup> As a result of this, even though C<sub>1</sub> is more sterically hindered than C<sub>3</sub>, alkyl halides of lower reactivity (higher selectivity) will preferentially react at the more nucleophilic methine site. On the other hand, as the reactivity of the alkyl halides is made increasingly higher, their selectivity will be lowered, and steric effects will begin to favor alkylation at the less hindered terminal site.

The above line of reasoning is strongly supported by the results of the alkylation reaction of the 1-(4-methoxyphenyl)-2-propanone dianion 31. With an electron-releasing substituent at the para position of the phenyl ring, it would be expected that the C<sub>3</sub> position in dianion 31 would bear a higher electron density than its counterpart in the 1-phenyl-2-propanone dianion 3; in turn, this should render the terminal position in the former intermediate more nucleophilic than in the latter. Indeed, alkylation of dianion 31 with 1-iodobutane afforded a substantially larger amount of the terminal alkylation product than dianion 3 (34% vs. 10%).

(8) (a) Levy, H.; Cope, A. C. *J. Am. Chem. Soc.* 1944, 66, 1684. (b) Young, W. G.; Kosmin, M.; Mixer, R. Y.; Campbell, T. W. *Ibid.* 1952, 74, 608. (c) Mixer, R. Y.; Young, W. G. *Ibid.* 1956, 78, 3379. (d) Herbrandson, H. F.; Mooney, D. S. *Ibid.* 1957, 79, 5809. (e) Ando, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* 1958, 31, 1026.

(9) For a discussion of the effects of substituents on electron density distribution in allylic anions, see: (a) Broadus, C. D. *Acc. Chem. Res.* 1968, 1, 231. (b) Hunter, D. H. In "Isotopes in Organic Chemistry"; Buncl, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1975; Vol. 1, pp 153-157.

(10) For a theoretical treatment of the electron density distribution in allylic anions, see: (a) Longuet-Higgins, H. C. *J. Chem. Phys.* 1950, 18, 265. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* 1952, 74, 3345.

(11) For a general discussion concerning the reactions of unsymmetrically substituted allylic anions with electrophilic reagents, see: Still, W. C.; Macdonald, T. L. *J. Org. Chem.* 1976, 41, 3620 and references cited therein.

(6) Sandel, V. R.; McKinley, S. V.; Freedman, H. H. *J. Am. Chem. Soc.* 1968, 90, 495.

(7) For studies showing that the negative charge in enolate anions resides largely on the oxygen atom, see: (a) Heiszwolf, G. J.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* 1967, 86, 807. (b) *Ibid.* 1970, 89, 1153.

The mode of alkylation of the 1,1-diphenyl-2-propanone dianion 4 can also be explained on the basis of the arguments developed above. The presence of two phenyl rings on C<sub>1</sub> would cause this position to bear a higher electron density but at the same time to be more sterically hindered than the corresponding position in the 1-phenyl-2-propanone dianion 3. The trend of the alkylation reactions of the 1,1-diphenyl-2-propanone dianion 4 (Table II) indicates that while this dianion behaves in a manner quite similar to that of 1-phenyl-2-propanone dianion 3, a definite increase in terminal alkylation products has taken place. It must be concluded, therefore, that steric effects play a much more dominant role in the alkylation reactions of dianion 4 than they do in dianion 3.

Unlike alkylations, the reaction of dianions 3 with *p*-anisaldehyde gave products resulting from terminal electrophilic attack, i.e., attack at the C<sub>3</sub> position. Although a detailed mechanism for this reaction is not presently available, it is noteworthy to point out that these results also parallel the reaction observed earlier in connection with the allylbenzene anion and related systems. Steric effects have been considered to be at least in part responsible for the observed mode of these reactions,<sup>12</sup> although a number of alternative mechanisms have also been proposed to explain the reactions of allylic anions with carbonyl compounds.<sup>13</sup>

Reaction of dianion 3 with water, deuterium oxide, methanol, ethanol, and ammonium chloride led invariably to protonation at the terminal carbon. The mode of proton attack on intermediate 3 is not entirely understood at this point. Initial proton attack at C<sub>1</sub> to give the less stable terminal enolate intermediate, followed by fast equilibration of the latter to the more stable enolate 7, seems unlikely in view of the results of the alkylation-silylation experiment described earlier. On the other hand, initial protonation on oxygen, with a subsequent rearrangement to the C<sub>3</sub>-protonated intermediate is a possibility, although it would be difficult to distinguish this mode of protonation from that involving direct electrophilic attack on C<sub>3</sub>.

## Experimental Section

**General Methods.** Melting points were taken on a Thomas-Hoover or Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gas chromatographic analyses (GC) were carried out on a Varian Aerograph Series 2700 gas chromatograph equipped with a thermal-conductivity detector and using helium as a carrier gas. A 5 ft × 0.25 in. column packed with 3% SE-30 on Varaport 30 was used. Infrared spectra (IR) were taken on a Beckman IR-8 or a Bausch and Lomb Spectronic 250 IR spectrophotometer. Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were obtained on a Varian Associates A-60 or EM360 spectrometer. Mass spectra were run on a Du Pont 21-490B mass spectrometer. Low-pressure preparative liquid chromatography separations were carried out using a 1 in. × 4 ft column packed with Merck 60 silica gel, preceded by a 1 in. × 10 in. scrubber column. Methylene chloride was used as the eluent.

**Formation of 1-Phenyl-2-propanone Potassium Enolate 7.** The potassium enolate 7 was generated by following a literature procedure<sup>14</sup> with some modifications. In general, potassium hydride, as a ca. 22% slurry in mineral oil, was weighed in the reaction flask and washed several times under an inert atmosphere with pentane or petroleum ether to remove the mineral oil. Dry THF was then added, and the reaction flask was connected to

a gas-collection manifold. 1-Phenyl-2-propanone was added via a glass syringe, and the hydrogen gas evolved was monitored. When gas evolution stopped, the formation of the enolate 7 was considered complete. The intermediate was then used as described below.

**Reaction of Potassium Enolate 7 with Iodomethane.** The enolate 7 (20 mmol) in 40 mL of THF, prepared as described above, was treated with 27 mmol of iodomethane in 20 mL of THF at 0–5 °C (ice bath). After 2 h the reaction mixture was neutralized with water (20 mL), the layers were separated, and the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure to give a yellow oil. Upon distillation, there was obtained 2.04 g (69%) of pure 3-phenyl-2-butanone (8): bp 68–70 °C (1.8 torr) [lit.<sup>15</sup> bp 106–110 °C (22 torr)]; IR 1704 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.35 (d, 3 H), 1.98 (s, 3 H), 3.74 (q, 1 H), 7.24 (s, 5 H); semicarbazone, mp 173–174 °C (lit.<sup>16</sup> mp 170–172 °C).

In a separate experiment, enolate 7 was generated as described above in THF, and its <sup>1</sup>H NMR was recorded: δ 7.31 (d, 2 H), 6.73 (t, 2 H), 6.28 (t, 1 H), 4.5 (s, 1 H). The region upfield from 4.0 ppm was obscured by mineral oil absorptions.

**Formation of 1-Phenyl-2-propanone Dianion 3.** A solution of 25 mmol of enolate 7 in 50 mL of THF was prepared as described above. The reaction mixture was then cooled to 0–5 °C (ice bath), and 29 mmol of *n*-butyllithium (1.6 M) in hexane was added dropwise via a glass syringe. Reaction occurred immediately to give the dark red 1-phenyl-2-propanone dianion 3. The solution was stirred for an additional 15–20 min, and it was then used as described below.

**<sup>1</sup>H NMR of Dianion 3.** The dianion 3 (0.53 g, 4.0 mmol) was prepared as described above in 3 mL of THF-d<sub>8</sub>/hexane, and its 60-MHz <sup>1</sup>H NMR was recorded with Me<sub>4</sub>Si as an external standard. The following absorptions were observed: δ 2.60 (br d, 2 H, terminal methylene protons), 3.82 (br s, 1 H, methine proton), 5.47 (br m, 1 H, *p*-C<sub>6</sub>H<sub>5</sub>), 6.33 (br m, 4 H, *o*- and *p*-C<sub>6</sub>H<sub>5</sub>).

**Reaction of Dianion 3 with *p*-Anisaldehyde.** 1-Phenyl-2-propanone (2.68 g, 20 mmol) was converted to its dianion 3 by using 20 mmol of KH and 24 mmol of *n*-butyllithium in 100 mL of THF. A solution of *p*-anisaldehyde (2.72 g, 20 mmol) in 30 mL of THF was then added dropwise at 0–5 °C, and the reaction mixture was stirred for 2 h. Water (50 mL) was then added, the layers were separated, and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure gave a red oil which crystallized upon trituration with pentane to give 2.20 g (44%) of 4-hydroxy-4-(*p*-methoxyphenyl)-1-phenyl-2-butanone (9). Recrystallization from benzene-petroleum ether gave a cream white solid: mp 78–79 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.80 (m, 2 H), 3.23 (br s, 1 H), 3.67 (s, 2 H), 3.77 (s, 3 H), 5.05 (t, 1 H), 7.3 (m, 9 H). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>: C, 75.56; H, 6.71. Found: C, 75.27; H, 6.74.

The hydroxy ketone 9 (1.50 g, 5.5 mmol) and *p*-toluenesulfonic acid monohydrate (0.25 g, 1.3 mmol) were dissolved in 75 mL of benzene and heated at reflux for 4 h. On cooling, the solution was washed with two 10-mL portions of aqueous NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure gave 0.90 g (65%) of 1-(*p*-methoxyphenyl)-4-phenyl-1-buten-2-one (5): mp 94–97 °C (lit.<sup>3</sup> mp 99–101 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.79 (s, 3 H), 3.90 (s, 2 H), 7.1 (m, 9 H).

**Sequential Treatment of Dianion 3 with 2-Bromopropane and Trimethylchlorosilane.** 1-Phenyl-2-propanone (7.0 g, 52.1 mmol) was converted to its dianion 3 by using 52.2 mmol of KH and 67.7 mmol of *n*-butyllithium in 60 mL of THF. A solution of 2-bromopropane (7.69 g, 62.5 mmol) in 20 mL of THF was then added dropwise at 0–5 °C, and the reaction mixture was brought up to room temperature. After 1 h of stirring, an ice bath was reinserted and trimethylchlorosilane (8.49 g, 78.2 mmol) was added. After 2 h of stirring at room temperature, the solvent was removed under reduced pressure to give a semisolid material which was extracted with pentane. Evaporation of the solvent afforded a yellow oil. GC analysis of the oil showed the presence of a single product. Distillation of the oil gave 10.1 g (78.2%) of the silyl enol ether 30: bp 65 °C (0.4 torr); *n*<sub>D</sub><sup>20</sup> 1.4830; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 0.00 (s, 9 H), 0.70 (d, 3 H), 1.05 (d, 3 H), 2.25 (m, 1 H), 2.74 (d,

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1 H), 4.04 (d of d, 2 H), 7.10 (m, 5 H); MS,  $m/z$  248 ( $M^+$ ). Anal. Calcd for  $C_{15}H_{24}OSi$ : C, 72.58; H, 9.67; Si, 11.29. Found: C, 72.42, H, 9.76; Si, 10.92.

**Protonation and Deuteration of Dianion 3.** 1-Phenyl-2-propanone (20–25 mmol) in 20 mL of THF was converted to its dianion 3 as described earlier and subsequently treated with 1 molecular equiv of the following proton donors: water, methanol, ethanol, ammonium chloride, and deuterium oxide. In all cases, the discharge of the bright red color of the dianion 3, and the conversion of the reaction mixture to the orange-red color of the enolate monoanion 7 were used as indicators. There was close agreement between the addition of 1 equiv of the proton donor and the color discharge. The  $^1H$  NMR spectra of the protonated (deuterated) reaction mixtures were essentially identical with that of the enolate monoanion 7 described earlier.

**Reaction of Dianion 3 with Alkyl Halides.** To a solution of dianion 3 (20–52 mmol) was added 1.2–1.5 equiv of the appropriate halide at ca. 5 °C. The reaction mixture was then allowed to reach room temperature, and stirring was continued for 2–4 h. Water was then added, the organic layer was collected and dried, and the alkylation product(s) was isolated by vacuum distillation. Specific details for each alkyl halide are given below.

**(A) Iodomethane.** Reaction of 20 mmol of dianion 3 with 27 mmol of iodomethane afforded a reaction mixture containing 3-phenyl-2-butanone (8) and 1-phenyl-2-butanone (15) in a ratio of 1.2:1.0 by GC and in an overall yield of 62%. The identity of products 8 and 15 were established by comparison with 3-phenyl-2-butanone (8) obtained from the methylation of monoanion 7, as described earlier, and 1-phenyl-2-butanone (15) prepared by a literature procedure.<sup>17</sup>

**(B) Iodoethane.** Reaction of 25 mmol of dianion 3 with 30 mmol of this alkyl halide afforded a reaction mixture containing 3-phenyl-2-pentanone (16) and 1-phenyl-2-pentanone (17) in a ratio of 5:1 by GC and in an overall yield of 65%. Distillation gave pure 3-phenyl-2-pentanone (16): bp 86–90 °C (3.3 torr) [lit.<sup>15</sup> bp 116–119 °C (23 torr)]; IR 1707  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.82 (t, 3 H), 1.93 (m, 2 H), 2.00 (s, 3 H), 3.58 (t, 1 H), 7.25 (s, 5 H); semicarbazone, mp 185–186 °C (lit.<sup>15</sup> mp 190–191 °C). The identity of 1-phenyl-2-pentanone (17) was established by comparison of its GC retention time and its  $^1H$  NMR absorptions in the original reaction mixture with those of an authentic sample.<sup>17</sup>

**(C) 1-Chloropropene.** Reaction of 52 mmol of dianion 3 with 62 mmol of 1-chloropropene afforded a reaction mixture containing 3-phenyl-5-hexen-2-one (18) and 1-phenyl-5-hexen-2-one (19) in a ratio of 8:1 by GC and in an overall yield of 66%. Distillation gave pure 3-phenyl-5-hexen-2-one (18):  $n_D^{19}$  1.5158 (lit.<sup>15</sup>  $n_D^{19}$  1.5158);  $^1H$  NMR ( $CCl_4$ )  $\delta$  1.93 (x, 3 H), 2.5 (m, 2 H), 3.66 (t, 1 H), 4.7–5.5 (3H), 7.2 (s, 5 H); 2,4-dinitrophenylhydrazone, mp 131–133 °C (lit.<sup>15</sup> mp 134–135 °C). The minor product 1-phenyl-5-hexen-2-one (19) was not isolated in a pure state; however, its mass spectrum obtained via GC/MS displayed characteristic peaks at  $m/z$  174 ( $M^+$ ), 119, 91, 83, 55.

**(D) 1-Iodobutane.** Reaction of 25 mmol of dianion 3 with 30 mmol of this halide afforded a reaction mixture containing 3-phenyl-2-heptanone (20) and 1-phenyl-2-heptanone (21) in a ratio of 9:1 by GC and in an overall yield of 57%. Distillation gave pure 3-phenyl-2-heptanone (20): bp 87–91 °C (1.3 torr) [lit.<sup>15</sup> bp 131–135 °C (16 torr)]; IR 1707  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.60–2.61 (m, 9 H), 2.00 (s, 3 H), 3.62 (q, 1 H), 7.25 (s, 5 H); semicarbazone, mp 151 °C (lit.<sup>15</sup> mp 156–157 °C). The identity of 1-phenyl-2-heptanone (21) was established by comparison of its GC retention time and  $^1H$  NMR spectrum with those of an authentic sample.<sup>17</sup>

**(E) 1-Chlorobutane.** Reaction of 25 mmol of dianion 3 with 30 mmol of 1-chlorobutane afforded 3-phenyl-2-heptanone (22) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 3-phenyl-2-heptanone (22): 70%; bp 89–94 °C (1.6 torr) [lit.<sup>15</sup> bp 131–135 °C (16 torr)]; IR 1707  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.61–2.61 (m, 9 H), 2.00 (s, 3 H), 3.62 (q, 1 H), 7.25 (s, 5 H); semicarbazone, mp 154–155 °C (lit.<sup>15</sup> mp 156–157 °C).

**(F) 2-Methyl-1-bromopropane.** Reaction of 25 mmol of dianion 3 with 30 mmol of 2-methyl-1-bromopropane afforded 5-methyl-3-phenyl-2-hexanone (23) as the only product, as shown

by GC analysis of the crude reaction mixture. Distillation gave pure 5-methyl-3-phenyl-2-hexanone (23): 72%; bp 81–85 °C (1.5 torr) [lit.<sup>15</sup> bp 119–124 °C (14 torr)]; IR 1705  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.73–2.55 (m, 9 H), 2.00 (s, 3 H), 3.75 (q, 1 H), 7.25 (s, 5 H); semicarbazone, mp 115–116 °C (lit.<sup>15</sup> mp 116–118 °C).

**(G) 2-Bromopropane.** Reaction of 25 mmol of dianion 3 with 30 mmol of 2-bromopropane afforded 4-methyl-3-phenyl-2-pentanone (24) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 4-methyl-3-phenyl-2-pentanone (24): 63%; bp 78–82 °C (2.2 torr); IR 1703  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.83 (q, 6 H), 2.02 (s, 3 H), 2.48 (m, 1 H), 3.58 (t, 1 H), 7.25 (s, 5 H); semicarbazone, mp 148–149 °C (lit.<sup>15</sup> mp 153–154 °C).

**(H) 2-Bromobutane.** Reaction of 25 mmol of dianion 3 with 30 mmol of 2-bromobutane afforded 4-methyl-3-phenyl-2-hexanone (25) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 4-methyl-3-phenyl-2-hexanone (25): 63%; bp 96–100 °C (3.6 torr); IR 1712  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.57–1.74 (m, 8 H), 2.03 (s, 3 H), 2.3 (m, 1 H), 3.52 (t, 1 H), 7.25 (s, 5 H); semicarbazone, mp 141–144 °C. Anal. Calcd for  $C_{14}H_{21}N_3O$ : C, 67.88; H, 8.56; N, 16.99. Found: C, 67.88; H, 8.58; N, 17.15.

**(I) (Bromomethyl)cyclohexane.** Reaction of 25 mmol of dianion 3 with 30 mmol of (bromomethyl)cyclohexane afforded 4-cyclohexyl-3-phenyl-2-butanone (26) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 4-cyclohexyl-3-phenyl-2-butanone (26): 73%; bp 117–121 °C (1.0 torr);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.55–2.24 (m, 13 H), 2.00 (s, 3 H), 3.79 (t, 1 H), 7.27 (s, 5 H); 2,4-dinitrophenylhydrazone, mp 122–123 °C (lit.<sup>18</sup> mp 126–127 °C).

**(J)  $\alpha$ -Chlorotoluene.** Reaction of 25 mmol of dianion 3 with 30 mmol of  $\alpha$ -chlorotoluene afforded 3,4-diphenyl-2-butanone (27) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 3,4-diphenyl-2-butanone (27): 52%; bp 115–120 °C (0.5 torr) [lit.<sup>15</sup> bp 119–122 °C (1.0 torr)]; IR 1704  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.89 (s, 3 H), 3.12 (m, 2 H), 3.90 (t, 1 H), 7.04 (s, 5 H), 7.17 (s, 5 H); 2,4-dinitrophenylhydrazone, mp 113–114 °C (lit.<sup>19</sup> mp 115–117 °C).

**(K) Bromocyclopentane.** Reaction of 25 mmol of dianion 3 with 30 mmol of bromocyclopentane afforded 1-cyclopentyl-1-phenyl-2-propanone (28) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 1-cyclopentyl-1-phenyl-2-propanone (28): 62%; bp 100–105 °C (1.1 torr) [lit.<sup>20</sup> bp 110–127 °C (2.5 torr)]; IR 1703  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.63–2.89 (m, 9 H), 2.03 (s, 3 H), 3.50 (t, 1 H), 7.26 (s, 5 H); 2,4-dinitrophenylhydrazone, mp 114–115 °C (lit.<sup>20</sup> mp 116–118 °C).

**(L) Bromocyclohexane.** Reaction of 25 mmol of dianion 3 with 30 mmol of bromocyclohexane afforded 1-cyclohexyl-1-phenyl-2-propanone (29) as the only product, as shown by GC analysis of the crude reaction mixture. Distillation gave pure 1-cyclohexyl-1-phenyl-2-propanone (29): 61%; bp 110–113 °C (1.1 torr) (lit.<sup>18</sup> bp 132–136 °C (2.5 torr)); IR 1712  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.56–2.00 (m, 11 H), 2.04 (s, 3 H), 3.36 (d, 1 H), 7.16 (s, 5 H); 2,4-dinitrophenylhydrazone, mp 151–152 °C (lit.<sup>21</sup> mp 155–156 °C).

**Formation of 1-(4-Methoxyphenyl)-2-propanone Dianion 31 and Reaction with 1-Iodobutane.** Dianion 31 was prepared by treatment of 1-(4-methoxyphenyl)-2-propanone (54.3 mmol) with an equivalent amount of potassium hydride in THF, followed by 65 mmol of *n*-butyllithium. 1-Iodobutane (54.3 mmol) was then added, and the reaction mixture was worked up as described earlier to give a mixture of 3-(4-methoxyphenyl)-2-heptanone (32) and 1-(4-methoxyphenyl)-2-heptanone (33) in a ratio of 1.9:1 by GC and in an overall yield of 73%. Distillation gave pure 3-(4-methoxyphenyl)-2-heptanone (32): bp 87–88 °C (0.02 torr);  $n_D^{23}$  1.5050;  $^1H$  NMR ( $CCl_4$ )  $\delta$  0.7–1.6 (m, 9 H), 1.6–2.0 (m, 2 H), 1.95 (s, 3 H), 3.48 (t, 1 H), 3.74 (s, 3 H), 6.93 (d of d, 4 H). Anal. Calcd for  $C_{14}H_{20}O_2$ : C, 76.36; H, 9.09. Found: C, 76.50; H, 9.09. The minor product 1-(4-methoxyphenyl)-2-heptanone (33) was iden-

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tified by comparison of its GC retention time and its  $^1\text{H}$  NMR spectrum with those of an authentic sample prepared as described below.

**Synthesis of 1-(4-Methoxyphenyl)-2-heptanone (33).** Compound **33** was synthesized from *p*-anisaldehyde and 1-nitrohexane by following the method of Heinzelman.<sup>22</sup> Thus, a mixture of 21.4 g (150 mmol) of *p*-anisaldehyde, 19.6 g (150 mmol) of 1-nitrohexane, and 3 mL of *n*-butylamine were refluxed vigorously; the mixture was then reduced with 30 g (54 mmol) of powdered iron and 54 mL of concentrated HCl in the presence of 0.6 g of  $\text{FeCl}_3$  to give **33**: bp 101–102 °C (0.02 torr);  $n_{\text{D}}^{25}$  1.5020;  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  0.7–2.0 (m, 11 H), 2.32 (t, 2 H), 3.48 (s, 2 H), 3.73 (s, 3 H), 6.90 (d of d, 4 H). Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_2$ : C, 76.36; H, 9.09. Found: C, 76.47; H, 9.30.

**Formation of 1,1-Diphenyl-2-propanone Dianion 4.** The following general procedure was used for the formation of 1,1-diphenyl-2-propanone dianion **4** throughout the present study.

To a stirred suspension of 30 mmol of KH in 25 mL of THF was added dropwise 20 mmol of 1,1-diphenyl-2-propanone in 20 mL of THF. After 30 min, the orange-yellow reaction mixture was cooled in a dry ice–acetone bath, and 30 mmol of 1.6 M *n*-butyllithium in hexane was added dropwise. The cooling bath was then removed, and the deep red reaction mixture was stirred for an additional 30 min. The dianion was then used as described below.

**Reaction of Dianion 4 with Alkyl Halides.** To a solution of 20 mmol of 1,1-diphenyl-2-propanone dianion in ca. 50 mL of THF, prepared as described above and cooled by means of an ice bath, was added 1.0–1.5 equiv of the appropriate halide. The reaction mixture was then allowed to reach room temperature, and stirring was continued for 18–24 h. Water was then added, the organic layer was collected and dried, and the alkylation products were isolated by low-pressure preparative liquid chromatography. Specific details for each alkyl halide are described below.

**(A) Iodomethane.** Reaction of dianion **4** with iodomethane (1.0 equiv) gave 1.82 g of 3,3-diphenyl-2-butanone (34%) and 1.61 g of 1,1-diphenyl-2-butanone (**35**) (77% overall yield). For **34**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.87 (s, 3 H), 2.10 (s, 3 H), 7.27 (s, 10 H); semicarbazone, mp 180–182 °C (lit.<sup>23</sup> mp 182 °C). For **35**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.05 (t, 3 H), 2.56 (q, 2 H), 5.12 (s, 1 H), 7.27 (s, 10 H); semicarbazone, mp 193–194 °C (lit.<sup>24</sup> mp 194–195 °C).

**(B) Bromoethane.** Reaction of dianion **4** with bromoethane (1.5 equiv) gave 1.63 g of 3,3-diphenyl-2-pentanone (**36**) and 2.53 g of 1,1-diphenyl-2-pentanone (**37**) (87% overall yield). For **36**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.69 (t, 3 H,  $\text{CH}_3$ ), 2.02 (s, 3 H), 2.38 (q, 2 H), 7.31 (s, 10 H); semicarbazone, mp 197–199 °C (lit.<sup>15</sup> mp 199–200 °C). For **37**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.86 (t, 3 H), 1.61 (m, 2 H), 2.52 (t, 2 H), 5.12 (s, 1 H), 7.27 (s, 10 H); semicarbazone, mp 190–191 °C (lit.<sup>25</sup> mp 191–192 °C).

**(C) 1-Chloropropane.** Reaction of dianion **4** with 1-chloropropane (1.5 equiv) gave 2.11 g of 3,3-diphenyl-2-hexanone (**38**) and 2.26 g of 1,1-diphenyl-2-hexanone (**39**) (87% overall yield). For **39**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.85 (m, 3 H), 1.41 (m, 4 H), 2.55 (t, 2 H), 5.14 (s, 1 H), 7.28 (10 H); 2,4-dinitrophenylhydrazone, mp 158–159 °C (lit.<sup>25</sup> mp 159 °C). For **38**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.90 (m, 5 H), 2.02 (s, 3 H), 2.29 (t, 2 H), 7.30 (s, 10 H); 2,4-dinitrophenylhydrazone, mp 171–172 °C (lit.<sup>15</sup> mp 174–175 °C).

**(D) 2-Bromopropane.** Reaction of dianion **4** with 2-bromopropane (1.5 equiv) gave 1.75 g of 3,3-diphenyl-4-methyl-2-pentanone (**40**) and 0.98 g of 1,1-diphenyl-4-methyl-2-pentanone (**41**) (54% overall yield). For **40**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.74 (d, 6 H), 1.97 (s, 3 H), 3.31 (m, 1 H), 7.31 (s, 10 H); mp 93–94 °C (from ethanol–water). Anal. Calcd for  $\text{C}_{18}\text{H}_{23}\text{O}$ : C, 85.67; H, 7.99. Found: C, 85.54; H, 8.14. For **41**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (d, 6 H), 2.12 (m, 1 H), 2.38 (m, 2 H), 5.10 (s, 1 H), 7.26 (s, 10 H) (lit.<sup>26</sup>  $^1\text{H}$  NMR identical with that of **42**).

**(E) 2-Chloropropane.** Reaction of dianion **4** with 2-chloropropane (1.5 equiv) gave 2.45 g of 3,3-diphenyl-4-methyl-2-pentanone (**40**) and 0.57 g of 1,1-diphenyl-4-methyl-2-pentanone (**41**) (60% overall yield). These products were identical in all respects with those obtained from the reaction of dianion **4** with 2-bromopropane.

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