# Notes

## Electron Spin Resonance Observations of Semidiones from Alkali Metal Reduction of 7-Norbornenone and 9-Benzonorbornenone[1]

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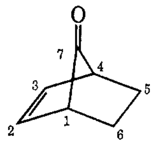
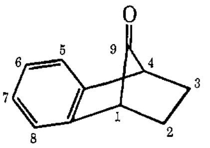
As part of our continued effort to study potentially nonclassical and homoaromatic species by esr,[4] attempts were made to prepare the ketyls[5] of 7-norbornenone (**1**) and 9-benzonorbornenone (**2**) by alkali metal reduction in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF).[7] Although radical anions are obtained, it appears that semidiones **3** and **4**, respectively, are formed. The ketyls **5** and **6** could not be detected. This result, to our knowledge, constitutes the first example of carbonyl insertion in the formation of semidiones from monoketones in this reduction medium.[8]



**1**



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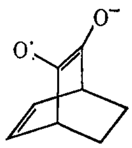

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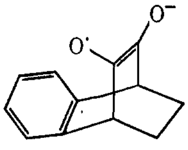

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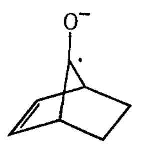

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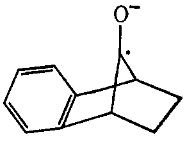
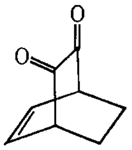
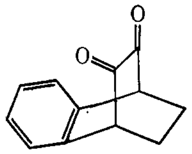


**6**

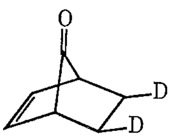
7-Norbornenone (**1**) in DME was treated with potassium, and the esr spectrum was resolved into a 1:2:1 triplet, $a_H = 2.69$ G (2 H). Each peak was further split into a 1:4:6:4:1 quintet, $a_H = 0.44$ G (4 H). The esr spectrum from potassium reduction of 9-benzonorbornenone (**2**) in DME consisted of a 1:2:1 triplet, $a_H = 2.35$ G (2 H), with additional small hyperfine splitting. The hyperfine-splitting constants obtained from the reduction products of **1** and **2** were found to be strikingly similar to those for the corresponding semidiones **3** and **4**, respectively, which were previously prepared by Russell, Holland, and Chang[9] from the diketones **7** and **8**. When **7** and **8** were reduced to semidiones **3** and **4**, respectively, under the same conditions used for reduction of **1** and **2**, identical hyperfine-splitting constants were indeed obtained.[10] The study of deuterio derivatives **9**, **10**, and **11** allows the assignment of values as in Table I.



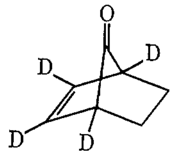
**7**



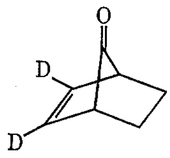
**8**



**9**

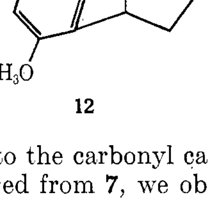


**10**



**11**

Taken alone, the hyperfine-splitting patterns do not permit differentiation between a semidione and its decarbonylated analog, a ketyl (*e.g.*, **3** and **5**).[9] However, the following data are consistent with semidione formation. Russell and coworkers[9] have measured hyperfine-splitting by $^{13}$C in natural abundance for the semidione **12**. For **12** in DME at 25° they found $a_C$ = 6.15 G (attributed to the carbonyl carbon).[11] For the semidione **3**, prepared from **7**, we observed $a_C$ = 6.12 G from $^{13}$C in natural abundance. As Russell has



**12**

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[1] This research was supported by a grant from the National Science Foundation.

[2] (a) Taken in part from the Ph.D. thesis of J. P. D., UCLA, 1969; National Science Foundation Trainee, 1965–1969. (b) Author to whom inquiries should be addressed at the Department of Chemistry, Yale University, New Haven, Conn. 06520.

[3] Deceased Nov 23, 1969.

[4] (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); (b) G. Moshuk, G. Petrowski, and S. Winstein, *ibid.*, **90**, 2179 (1968).

[5] In this paper the term ketyl is restricted to one-electron reduction products of monoketones, whereas one-electron reduction products of conjugated diketones will be referred to as semidiones.[6]

[6] G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, pp 87–150.

[7] During the course of this investigation the nature of the 7-norbornenyl and 9-benzonorbornenyl radicals were reported: (a) J. Warketin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968); (b) G. A. Russell and G. W. Holland, *ibid.*, **91**, 3968 (1969); and (c) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969).

[8] (a) For an excellent review of a wide variety of semidione preparations see ref 6. Russell[6] has suggested that a carbonyl insertion reaction occurs in the electrolytic reduction of acetophenone at high electrode potentials in dimethylformamide (DMF), forming the 1-phenylpropane-1,2-semidione. Russell[6] has speculated that the additional carbonyl group comes from the DMF. A similar example of carbonyl insertion has recently been reported in the electrolysis of 3,4,5-trimethoxybenzaldehyde in DMF: C. Corvaja, P. L. Nordio, and G. Giacometti, *J. Amer. Chem. Soc.*, **89**, 1751 (1967). (b) We have just learned from Professor G. A. Russell that he and his coworkers have recently observed results similar to those reported here. For example, they have found that the ketyl of 2,2,4,4-tetramethylcyclobutanone, obtained by potassium reduction in THF, undergoes carbonyl insertion at −50° forming the 3,3,5,5-tetramethylcyclopentan-1,2-semidione.

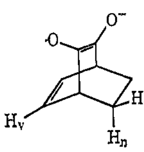
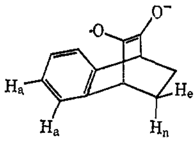
[9] G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967).

[10] Reduction of **2** and **8** in DME with sodium gave rise to identical 1:1:1:1 quartet splitting due to one sodium atom as well, $a_{Na} \approx 0.7$ G.

[11] E. T. Strom and G. A. Russell, *J. Chem. Phys.*, **41**, 1514 (1964).

Table I

Observed Hyperfine Splitting Constants[a]

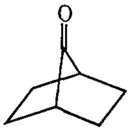
| Structure | Precursor | Reagent | Solvent | $H_e$ | $H_n$ | $H_v$ |
|---|---|---|---|---|---|---|
|  | 1 | Potassium | DME | 0.44 | 2.69 | 0.44 |
| | 1 | Potassium | THF | 0.41 | 2.59 | 0.41 |
| | 7 | Potassium | DME | 0.46 | 2.68 | 0.46 |
| | 7[b] | Enolate anion of propiophenone | DMSO | 0.41 | 2.60 | 0.41 |
| | | | | $H_e$ | $H_n$ | $H_a$ |
|  | 2 | Potassium | DME | *c* | 2.35[d] | *c* |
| | 8 | Potassium | DME | *c* | 2.35 | *c* |
| | 8 | Sodium[e] | DME | 0.18 | 2.35 | 0.09 |
| | 8[b] | Enolate anion of propiophenone | DMSO | 0.20 | 2.35 | 0.09 |

[a] All values are in gauss. The bridgehead hydrogens (in the nodal plane of the $p_z$ orbital) give rise to no detectable splitting.[9] [b] These values are taken from the work of Russell, Holland, and Chang.[9] [c] Small hyperfine splitting was observed, but the multiplicity could not be determined (0.09-G peak separation). [d] This value was assigned to the endo proton by analogy with the corresponding radical anion from the diketone.[9] [e] The value for $a_{Na}$ is 0.73 G at −20°.

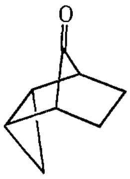
pointed out,[9] these values appear to exclude ketyl structures, where a value of $a_C^{CO}$ approaching 50 G would be expected.[12] Unfortunately, it was not possible to obtain $a_C$ values for the reduction products prepared from the monoketones, because the signal intensities were not high enough to observe hyperfine splitting by $^{13}C$ in natural abundance.

Two additional, although less conclusive, arguments can be presented in support of semidione formation from reduction of the monoketones **1** and **2**. The signal amplitude necessary to observe the radical anions was a factor of 100 or greater in the case of those generated from the monoketones, compared with those generated from the diketones. This is consistent with a secondary reduction product being formed from the monoketones in low yield. Secondly, the radical anions generated in this study were stable for hours at room temperature. In fact, the reduction product from **1** showed a 1:2:1 triplet even after 6 days at 8°. To our knowledge ketyls do not possess such stability.[13]

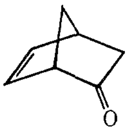
Attempts were made to obtain the radical anions of several compounds that are related to 7-norbornenone. However, no esr signal was detected when either **13**, **14**, or **15** in DME was treated with potassium.



**13**

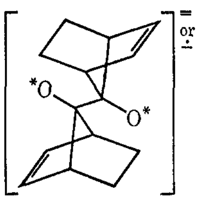


**14**



**15**

The present study affords no evidence concerning the detailed mechanism of this unusual conversion (*i.e.*, **1** to **3**). One possible means of forming the semidione **3** from the monoketone **1**, which can be visualized, involves rearrangement of the dimer **16** to give **3** and cyclohexadiene. Some support for this scheme comes from a set of known equilibria involving aliphatic ketyls and the corresponding dimers.[13] However, no esr signal was detected for any known by-products of this rearrangement.[14,15]



**16**
(asterisks equal
- or ·)

### Experimental Section

**General.**—Nmr spectra were obtained in carbon tetrachloride using a Varian Associates Model A-60 spectrometer with tetramethylsilane (τ 10.0) as the internal standard unless otherwise specified. Gas-liquid chromatography (glpc) was performed on a Varian-Aerograph A-90-P instrument, employing the following column: 6.0 ft × 0.25 in. 20% XF 1150 on Chromosorb W, nonacid washed 60–80 mesh. Ir spectra were recorded in carbon tetrachloride on a Perkin-Elmer 421 instrument.

**7-Norbornenone** (**1**). A.—This compound was prepared according to the procedure of Gassman and Pape[16] and was purified by preparative glpc: ir 1770 cm$^{-1}$ (C=O); nmr τ 3.50 (t, 2 H, olefinic protons), 7.23 (m, 2 H, bridgehead protons), 8.09 (m, 2 H, exo C-5 and C-6 protons), and 8.87 (m, 2 H, endo C-5 and C-6 protons). *Anal.* Calcd for $C_7H_8O$: C, 77.75; H, 7.46. Found: C, 77.80; H, 7.57.

B.—Ketone **1** was also prepared by Oppenauer oxidation[17] of 2-norbornen-7-(*anti*)-ol.[18]

***exo*,*exo*-5,6-Dideuterio-2-norbornen-7-one** (**9**) was prepared by Oppenauer oxidation[17] of *exo*,*exo*-5,6-dideuterio-2-norbornen-7-(*anti*)-ol.[19] The product was purified by preparative glpc: ir 1770 cm$^{-1}$ (C=O); nmr τ 3.47 (t, 2 H, olefinic protons), 7.25 (t, 2 H, bridgehead protons), and 8.82 (broad singlet, 2 H, endo C-5 and C-6 protons). This spectrum indicated that exo C-5 and C-6 positions contained ≥95% D.

**1,2,3,4-Tetradeuterio-2-norbornen-7-one** (**10**) was prepared using the Gassman and Pape[16] procedure for **1** with the exception

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[12] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960).

[13] N. Hirota, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, pp 35–85.

[14] A 1:1 doublet ($a$ = 15.2 G) was detected upon potassium reduction of **1** in DME or THF that was symmetrically disposed about the 1:2:1 triplet. At 25° this doublet disappeared within *ca.* 2 hr, whereas the triplet remained unchanged. The species giving rise to this doublet is unknown. Such a doublet was not observed in the reduction of **2**.

[15] The possibility that the CO moiety arises from solvent, though remote, cannot be excluded.

[16] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[17] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

[18] P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

[19] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

that *tert*-BuOD was used instead of *tert*-BuOH in the dechlorination of 7,7-dimethoxy-1,2,3,4-tetrachloro-2-norbornene. The ketone was purified by preparative glpc: ir 1770 cm$^{-1}$ (C═O); nmr τ 8.05 (m, 2 H, exo C-5 and C-6 protons) and 8.83 (m, 2 H, endo C-5 and C-6 protons). This spectrum indicated ≥95% D at all C-1, C-2, C-3, and C-4 positions.

**2,3-Dideuterio-2-norbornen-7-one (11).**—The vinyl protons of 7,7-dimethoxynorbornene[16] were exchanged with lithium cyclohexylamide-*N*-D and cyclohexylamine-*N*-$D_2$[20] at 25°. The ketal was purified by preparative glpc. The nmr spectrum indicated *ca.* 1.4 atom D per molecule in the olefinic region (τ 4.00), and only the vinyl protons were exchanged under these conditions. Mass spectral analysis (AEI Model MS 9) indicated that the total atom D per molecule was 1.38. The deuterio ketal was converted to 11 in the normal manner[16] and purified by preparative glpc: ir 1770 cm$^{-1}$ (C═O); nmr indicated *ca.* 1.4 atom D per molecule in the olefinic region (τ 3.48).

**7-Norbornanone (13).**—Hydrogenation of 1 according to the procedure of Gassman and Pape[16] gave 13: mp 77–79° (lit.[16] mp 79.5–80.5°); ir 1785 cm$^{-1}$ (C═O); nmr ($CS_2$, external TMS) showed a multiplet at τ 7.80–8.60.

*endo*-**Tricyclo[3.2.1.0$^{2,4}$]octan-8-one (14)** was obtained from M. A. Battiste[21] and was purified by preparative glpc: mp 62–69° (lit. mp 58–61°[21] and 71–72°[22]); ir 1760 cm$^{-1}$ (C═O); nmr (external TMS) τ 7.78 (m, 2 H) and 8.0–9.3 (m, 8 H).

**2-Norbornenone (15)** was obtained from R. K. Lustgarten and was purified by preparative glpc: nmr τ 3.48 (m, 1 H, olefinic proton), 3.90 (m, 1 H, olefinic proton), 6.85 (m, 1 H, bridgehead proton), 7.10 (m, 1 H, bridgehead proton), and 7.68–8.37 (m, 4 H).

**9-Benzonorbornenone (2).**—Oxidation of *anti*-9-benzonorbornenol[17] in the same manner as that described by Bartlett and Giddings[17] led to the desired product, which was purified by preparative glpc: ir 1770 cm$^{-1}$ (C═O); nmr τ 2.82 (broad peak, 4 H, aromatic protons), 6.78 (m, 2 H, bridgehead protons), 7.92 (m, 2 H, exo C-2 and C-3 protons), and 8.76 (m, 2 H, endo C-2 and C-3 protons). *Anal.* Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.49; H, 6.27.

**Esr Spectra.**—The radical anions were prepared under vacuum (*ca.* 0.1 μ) by the reduction of ketones and diketones with alkali metals using standard procedures described elsewhere.[2a] All reactions were carried out in a sealed-off glass apparatus that included a cell for esr measurement. Esr spectra were obtained with a Varian 4502 spectrometer with a "field dial" using 100-kc field modulation. Low-temperature experiments were made using a Varian variable-temperature control unit. The temperature reading was found to be accurate within ±3°. Hyperfine frequencies were calibrated using a Harvey-Wells proton gaussmeter and a Beckman frequency counter.

**A. Reduction of 7-Norbornenone (1).**—The ketone (10 mg) in DME (*ca.* 2.5 ml) was treated with potassium at −78°. The solution became yellow-orange at 25° and the esr spectrum was resolved into a 1:2:1 triplet, $a_H$ = 2.69 G (2 H). Each peak was further split into a 1:4:6:4:1 quintet, $a_H$ = 0.44 G (4 H). A 1:1 doublet ($a$ = 15.2 G) was detected that was symmetrically disposed about the center peak and slightly less intense.[14] The use of THF instead of DME as solvent gave similar results at 25°, $a_H$ = 2.59 G (2 H) and $a_H$ = 0.41 G (4 H). A 1:1 doublet, $a$ = 15.2 G, was also observed. When the ketone (10 mg) in DME (*ca.* 2 ml) was treated with sodium at 25°, only a single peak (width *ca.* 13 G) was detected. All attempts to obtain a resolved spectrum at temperatures ranging from −80 to 50° failed.

**B. Reduction of 9, 10, and 11.**—The ketones in DME were treated with potassium at −78°. The following values were obtained at 25°: from 9, $a_H$ = 2.69 G (2 H) and $a_H$ = 0.44 G (2 H); from 10, $a_H$ = 2.65 G (2 H) and $a_H$ = 0.46 G (2 H); and from 11, $a_H$ = 2.68 G (2 H) and $a_H$ = 0.4 G (2 H).

**C. Attempted Reduction of 13, 14, and 15.**—The ketones in DME were treated with potassium at −78°. No esr signals were observed at temperatures ranging from −78 to 25°. The results were the same when the solutions were maintained at 25° for several hours.

**D. Reduction of Bicyclo[2.2.2]oct-5-ene-2,3-dione (7).**—The diketone[9] (1 mg) in DME (*ca.* 1.5 ml) was treated with potassium at 25°. The spectrum was well simulated using values of $a_H$ = 2.68 G (2 H) and $a_H$ = 0.46 G (4 H). Additional hyperfine splitting of $a$ = 0.1 *G* was also observed, but it was not possible to determine the multiplicity. This hyperfine splitting is most likely due to the potassium cation. When the signal level was increased by a factor of 100, the hyperfine splitting by $^{13}$C in natural abundance was easily observed. The value obtained, $a_C$ = 6.12 G, is attributed to the carbonyl carbon.[11]

**E. Reduction of 9-Benzonorbornenone (2).**—The ketone (25 mg) in DME (*ca.* 3.5 ml) was treated with potassium at −78°. The best resolved spectra were recorded at −40°, where a 1:2:1 triplet, $a_H$ = 2.35 G (2 H), was observed. Each peak was split into 11 additional peaks and possibly more, with a separation of 0.09 G. Some of this additional hyperfine splitting is most likely due to the potassium cation. In another experiment, the ketone (10 mg) in DME (*ca.* 2 ml) was treated with sodium at 25°. At −40° the relative intensities of the various lines were in accord with a triplet splitting of $a_H$ = 2.35 G (2 H) and a 1:1:1:1 quartet splitting of $a_{Na}$ = 0.7 G (1 Na).

**F. Reduction of Benzobicyclo[2.2.2]oct-5-ene-2,3-dione (8).**—The diketone[9] (2 mg) in DME (*ca.* 2 ml) was treated with potassium at 25°, and a triplet, $a_H$ = 2.35 G (2 H), was observed. Additional splitting, as found in the reduction of 2, was detected. In another experiment, the diketone (2 mg) in DME (*ca.* 3 ml) was treated with sodium at 25°. The best resolved spectra were recorded at −20°, where the following values were obtained: $a_H$ = 2.35 G (2 H), $a_{Na}$ = 0.73 G (1 Na, 1:1:1:1 quartet splitting), $a_H$ = 0.18 G (2 H), and $a_H$ = 0.09 G (4 H).

**Registry No.**—**1**, 694-71-3; **2**, 6165-88-4; **3**, 17441-59-7; **4**, 17441-60-0; **7**, 17547-68-1; **8**, 17547-69-2; **9**, 28610-76-6; **10**, 28610-77-7; **11**, 28610-78-8.

**Acknowledgment.**—The following substances were obtained as gifts: 14 from Professor M. A. Battiste;[21] 15 from Dr. R. K. Lustgarten; and 7 and 8 from Professor G. A. Russell.[9] We are grateful to Professor Russell, who made available information prior to publication and provided helpful discussion.

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[20] A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *ibid.*, **84**, 244 (1962).

[21] M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

[22] H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967).

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# Reactions of Some Methylene Ketones with Dimethyl Phthalate. A New Route to 2-Substituted 1,3-Indandiones

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The reactions of methyl ketones with dialkyl phthalates to yield 2-acyl-1,3-indandiones have been the object of several investigations.[1–3] The present note describes the reactions of ketones containing one or two methylene groups adjacent to the carbonyl, hereafter called methylene ketones, with dimethyl phthalate (**1**). Symmetric and unsymmetric methylene ketones have been condensed with **1** in the presence of sodium methoxide or sodium hydride. 3-Pentanone and 4-heptanone gave respectively 2-methyl- and 2-ethyl-1,3-indandione. The mechanism shown in Scheme I is

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[1] E. Schwerin, *Chem. Ber.*, **27**, 104 (1894).

[2] L. B. Kilgore, J. Ford, and W. C. Wolfe, *Ind. Eng. Chem.*, **34**, 494 (1942).

[3] S. Shapiro, K. Geiger, and L. Freedman, *J. Org. Chem.*, **25**, 1860 (1960).