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Chemical Trapping of 1,4-Biradicals with Hydrogen and Deuterium Selenides

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1,4-Biradicals photogenerated from alkyl phenyl ketones have been trapped directly by hydrogen selenide before the biradicals undergo usual collapsing. Two hydrogen atoms are thus introduced into both radical sites. The rate constant for hydrogen abstraction of secondary carbon radicals from H_2Se has been estimated to be greater than $1.6 \times 10^8\ M^{-1}s^{-1}$.

Biradicals may be the most commonly invoked intermediates in organic photochemistry, and trapping of these short lived biradicals has been of current interest.[1)] We have shown that hydrogen selenide has a remarkable hydrogen donating ability toward photoexcited carbonyls and ketyl radicals as well as other radical intermediates in the Norrish Type I reaction.[2,3)] In the presence of hydrogen selenide, carbonyl compounds undergo photoreduction in an unusual way to give corresponding alcohols without formation of pinacols. We report here that hydrogen selenide (H_2Se) and deuterium selenide (D_2Se) efficiently trap both sites of 1,4-biradicals generated through the Norrish Type II process from alkyl phenyl ketones. Direct trapping of both sites of such biradicals has never been attained to the best of our knowledge.

It is well known that photolysis of butyrophenone derivatives **1** in methanol gives Type II products **5** and **6** via corresponding 1,4-biradical intermediate **4** with the total quantum yield of 1.0 (Scheme 1).[4)] When **1** was irradiated in the presence of D_2Se, formation of Type II products was greatly suppressed and corresponding

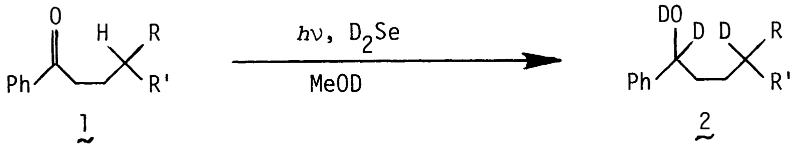
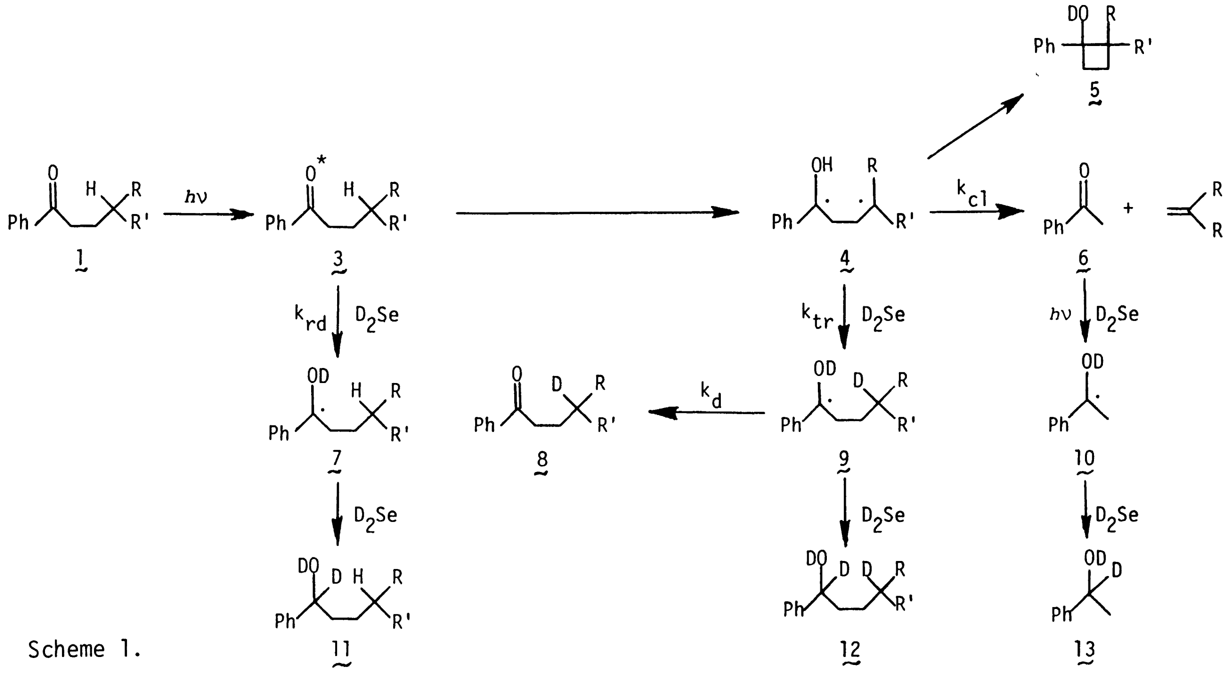


Table 1. Labeling experiment of 1,4-biradicals with D_2Se

Product	R	R'	τ_K	τ_{BR}	d-Content of 2		Yield
			ns	ns	1-position	4-position	%
2a	H	H	279[a)]	157±79[a)]	0.98	0.36±0.12	67
2b	H	Me	≦12[6d)]	103±7[6d)]	0.97	1.29±0.04	58
2c	Me	Me	4.7[6b)]	97±10[6c)]	0.98	0.84±0.01	54

a) Estimated value from τ_K and τ_{BR} in wet acetonitrile, see Ref. 6b.



Scheme 1.

alcohol **2** was obtained as the major product in which deuterium was incorporated.5)

In Table 1 are listed average deuterium contents at 1- and 4-positions and isolated yields of the products **2a-c** together with lifetimes of triplet carbonyls τ_K's and those of biradicals τ_{BR}'s derived from parent ketones **1a-c**.6) Trapping of 1,4-biradical intermediates **4** is evident from deuterium incorporation at the 4-position. Deuterium contents at the 4-position vary depending on the substituents, but those at the 1-position are consistently close to unity in any cases. Based on these results and evidences obtained previously,2,3) we can postulate Scheme 1 for the behavior of **1** in the present reaction system. High deuterium content at the 4-position of **2c** indicates that reaction of triplet carbonyl **3c** with D_2Se giving rise to **11c** is a minor path in the case of **1c** under the reaction conditions. On the contrary, this process became predominant in the case of **1a** because of relatively much longer lifetime of the triplet carbonyl **3a**. The fact that deuterium content at the 4-position of **2b** is more than unity suggests that some decay process such as **9** to **8** may exist. If **8** is formed, similar photoinitiated reaction with D_2Se may give **2** which contains more than one deuterium at the 4-position in cases of **2a** and **2b**. The present reaction system is the first example where trapping occurs at the both sites of Type II biradicals. Similar labeling experiments with octanethiol gave only γ-deuterated ketones **8** and pinacols (coupling products of **9**) as the trapped products.7) The use of tributyltin deuteride did not lead to deuterium incorporation because of its fast interaction with triplet carbonyl **3**.7)

The use of H_2Se instead of D_2Se gives corresponding alcohol **14** (corresponding to **11** and **12** in Scheme 1 where D=H), acetophenone **6**, and 1-phenylethanol **15**. Formation of these three products from **1c** was monitored by GLC and plotted in Fig. 18) which does not contradict the proposed reaction scheme; i.e., **14c** and **6** were formed as the primary products and then **6** was reduced to **15**. Quite slow formation of **15** at the early stage of the reaction may be attributed to efficient energy transfer from triplet acetophenone to the remaining 1c.[9] Similar figures were obtained in the cases of 1a and 1b.

Since the behavior of these type II biradicals reflects reactivities of corresponding monoradicals,[1,7] rate of biradical trapping with H_2Se corresponds to the reaction rate of H_2Se toward carbon radicals having the same substituent(s) at the radical center.[1,7,10] With a hypothesis that the reaction of H_2Se with carbon radicals is first order on each component and under the conditions where k_{rd} and k_d are negligible,[8] the product ratio 14/(6 + 15), i.e., 12/(6 + 13) in Scheme 1 where D=H, corresponds to $k_{tr}[H_2Se]/k_{cl}$. Three ketones 1a-c gave the product ratios of 5.47, 2.27, and 2.51, respectively. In the case of 1a, the direct reduction of triplet carbonyl could not be ruled out due to its remarkably long triplet lifetime leading to the appreciably larger product ratio than in cases of 1b and 1c. In the case of 1b, from the value of 2.27 together with the reported τ_{BR} and quantum yield $\phi_{cl}=0.70$ of the biradical cleavage process,[11] k_{tr} was calculated to be 1.6×10^8 $M^{-1}s^{-1}$. Since the rate constant k_d of the decay process is unknown and so contribution of the process was ignored in the above calculation, the obtained value corresponds to the lower limit of the hydrogen abstraction rate constant from H_2Se by secondary carbon radicals.[8] This value is quite large in comparison with the reported reaction rate constants of carbon radicals with thiols[7,10a,12] and tin hydrides.[7,13]

In summary, we have shown an example which demonstrates high potentiality of H_2Se and D_2Se as radical trapping agents. Hydrogen and deuterium selenides will be applicable to trapping of a variety of radicals. Especially, labeling experiment using D_2Se will provide fundamental informations in probing the structure and reactivity of the transient radical intermediates.

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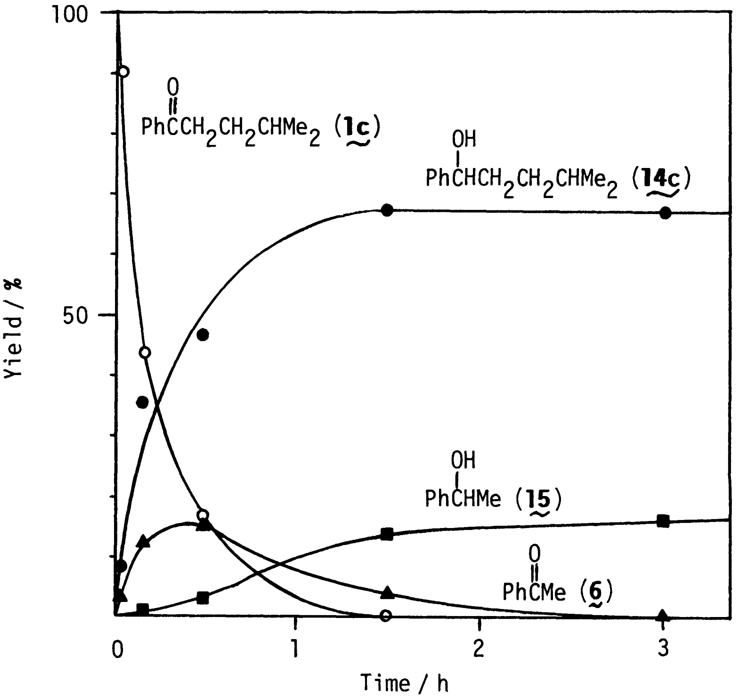

Fig. 1. Photolysis of γ-methylvalerophenone (1c) in the presence of hydrogen selenide in methanol.

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5) Labeling experiment with D_2Se: In a 10 mm diameter Pyrex reaction tube, a solution of γ-methylvalerophenone **1c** (158 mg, 0.3 M) and deuterium selenide (D_2Se, 0.5 M) in MeOD (d-content 99%, 3 ml) was irradiated at 20 °C for 24 h with a high pressure mercury lamp (300 W). After air oxidation of remaining D_2Se, deposited selenium was filtered. The product was washed with water and extracted into ether. Evaporation and column chromatography (silica gel/ benzene) followed by distillation (1 mmHg) gave 88 mg of **2c** (54%). From integration on ^{1}H-NMR using Eu(DPM)$_3$ (europium tris(2,2,6,6,-tetramethyl-3,5-heptanedionate)) as a shift reagent, deuterium contents at 1- and 4-positions were calculated to be 98% and 83±1%, respectively, taking the deviation of the integration as 5%.

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8) In order to minimize the contribution of direct reduction of triplet carbonyl **3** with H_2Se and to obtain comparable amounts of Type II products, the reaction was performed under dilute conditions, i. e., a methanol solution of ketone **1** (0.05 M) and hydrogen selenide (0.1 M). Formation of corresponding alcohol **14**, acetophenone **6**, 1-phenylethanol **15** was monitored by GLC (PEG-HT, 5%, 4 m, 180 °C). Final GLC yields of **14a-c** were 82%, 81%, and 66%, respectively.

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