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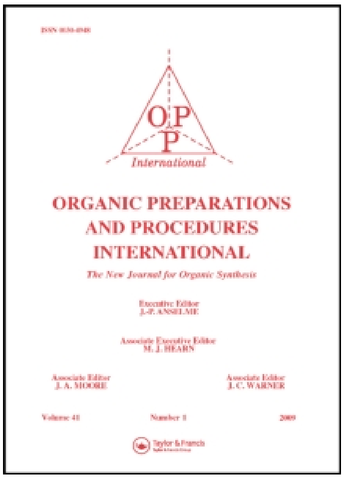

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# 9-Alkyl-9-Fluorenols From 9-Fluorenone Dianion

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# OPPI REPORTS

(by John L. Ferrari, Associate Editor)

## 9-Alkyl-9-Fluorenols From 9-Fluorenone Dianion

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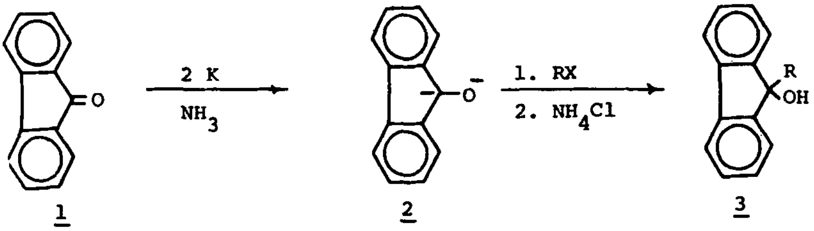

1 2 3

R= a) $CH_3$, b) $C_2H_5$, c) n-$C_4H_9$, d) $CH_2$=$CHCH_2$, e) $PhCH_2$, f) H

The authors extend an earlier reported route[2a,b] to give an alternate procedure to the Grignard method[3,4] for alkylation of 9-fluorenone *via* the hitherto unreported 9-fluorenone dianion. The following known carbinols (3) were prepared (percent yield, m.p., recrystallization solvent given): 3a from methyl iodide: (67), (175-176°), benzene-hexane; 3b from ethyl bromide: (47), (100-101°), cyclohexane; 3c from n-butyl bromide: (67), (129-131°), hexane; 3d from allyl bromide: (60), (118-120°), benzene-hexane; 3e from benzyl chloride: (69), (143-145°), benzene-hexane; 3f from ammonium chloride: (98), (155-157°), water. The reaction failed to afford the desired products with isopropyl

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bromide and tert- butyl chloride.

## EXPERIMENTAL[5]

Preparation of Dianion 2 A 500 ml, three-necked flask fitted with a mechanical stirrer, addition funnel, and Dry Ice condenser was heated for 10 min with a free flame while being swept with a stream of dry nitrogen. Ammonia (250 ml), which had been pre-dried with sodium, was then distilled into the reaction flask. Potassium metal (1.1 g, 0.028 g-atom) was then added and stirring begun. After 5 min 2.5 g (0.014 m) of solid 9-fluorenone (1) was introduced through a powder funnel and the resulting solution was allowed to stir for 30 min under nitrogen. At the end of this time the orange-brown reaction mixture, which was assumed to contain 0.014 mole of dianion 2, was used in the experiments.

9-Methyl-9-fluorenol 3a Dianion 2 was methylated with one equivalent of methyl iodide as a 10% v/v solution in anhydrous ether. After 30 minutes the reaction was quenched with a five-fold molar excess of solid ammonium chloride cautiously added. After an aqueous work up the solid residue was recrystallized from benzene-hexane (ca. 1:1) to give 1.83 g (67%) of 9-methyl-9-fluorenol as white prisms.

## REFERENCES

1. (a) Abstracted from the Ph.D. dissertation of J. A. Campbell, VPI & SU, August 1970. (b) To whom inquiries should be addressed.

2a. C. B. Wooster, J. Am. Chem. Soc., 50, 1388 (1928); P. J. Hamrick, Jr. and C. R. Hauser, ibid., 81, 493 (1959).

2b. See S. Selman and J. F. Eastham, J. Org. Chem., 30, 3804 (1965) and references cited therin, for a description of related 1,2-dianions derived from diaryl ketones.

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3. For representative examples see, (a) C. L. Arcus and E. A. Lucken, J. Chem. Soc., 1634 (1955); (b) Y. Sprinzak, J. Am. Chem. Soc., 74, 2116 (1952); (c) W. Schlenk, Chem. Ber., 64, 742 (1931).

4. G. Wittig, H. Doser and I. Lorenz, Ann., 562, 192 (1949) have reported the isolation of certain carbinols of type 3 by rearrangement of 9-fluorenyl ethers with phenyllithium. This method, which is less convenient than either the Grignard procedure or the present approach has apparently seen little synthetic use.

5. All chemicals were commercial reagent grade and were used without purification. Melting points were taken on a Thomas-Hoover apparatus in open capillaries and are corrected.

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## Convenient One-Step Dialkylation of Diethyl Malonate With Sodium Hydride

Submitted by: Edwin M. Kaiser, Janet A. Fries
and Walter J. Simonsen, Jr.
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The authors describe the title procedure using sodium hydride in tetrahydrofuran (THF). Thus, the di-*n*-butyl (86%), di-*n*-octyl (66%), dibenzyl (98%) and di-2-phenethyl(49%) diethyl malonates were obtained in the given yields from the respective halides.[1] Cyclizations using 1,4-dibromobutane and 1,3-dibromopropane afforded the cyclopentyl (I 63%) and