CALCIUM, STRONTIUM AND BARIUM

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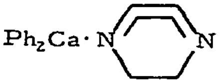
Diarylcalcium reagents have been prepared by metal displacement from diarylmercurials (1):

$$Ar_2Hg + Ca \xrightarrow[(76-98\%)]{THF} Ar_2Ca + Hg$$

$(Ar = Ph, m\text{-}MeC_6H_4, 1\text{-}C_{10}H_7, PhCH_2)$

The calcium must be activated by amalgamation in order to obtain successful reaction. The Ar_2Ca compounds were characterized by hydrolysis and their reactions with CO_2 to give $ArCO_2H$. Also, diphenylcalcium was isolated as a complex with DABCO:



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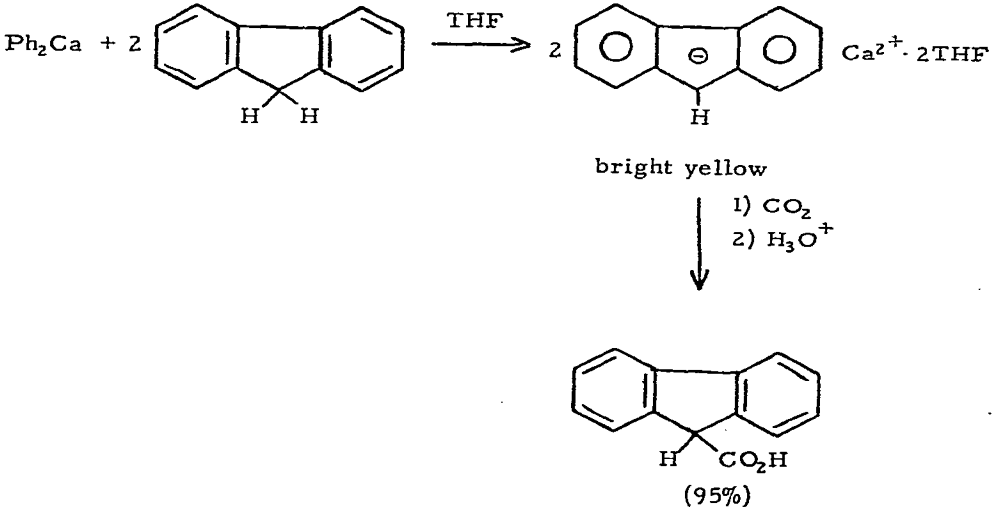
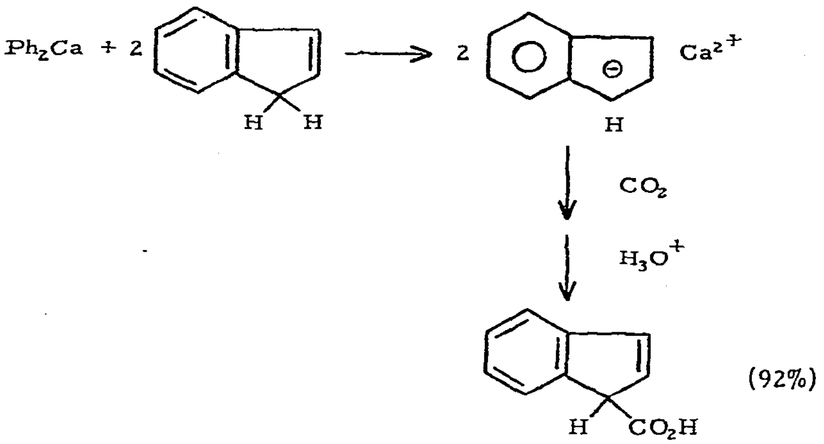
which reacts exothermally with water and is pyrophoric in air. Another report of a similar process in which the calcium was activated mechanically by grinding a silicone oil slurry has appeared (2). Tetrahydrofuran solutions of diallylcalcium and various dialkylcalciums (R_2Ca, $R = C_1 - C_{25}$) were prepared from the respective mercurials. Diallylcalcium was isolated as a pyrophoric powder.

The RI + Ca reaction has been the subject of further study by French and Russian groups. n-Hexyl iodide was found to react with calcium metal in THF to give some n-hexylcalcium iodide, but n-dodecane was the major product (3). It is believed that both products result from radical processes. A Russian group has studied in detail the variables which affect the RX + Ca reaction (4): solvent, organic halide used, method of calcium activation, reactant stoichiometry. The best solvents are diethyl ether and THF; RI is greatly preferred over RBr or RCl; iodine activation of calcium turnings was claimed to be the best procedure. But even under the best conditions, the RCaI yields reported were only 10-37%, probably because of the competitive coupling reaction. On the other hand, another Russian group who activated their calcium by treatment with mercuric chloride or with iodine reported significantly better yields (39-62%) of RCaI (R = Me, Et, n-Pr) in RI + Ca reactions carried out in Et_2O or THF (5). Clearly, reaction conditions for the RI + Ca reaction need to be more precisely defined.

Metalation reactions have served in the preparation of calcium derivatives of the more acidic hydrocarbons (6,7):





PhCaI·DABCO, $\boxed{1}$, was less effective as a metalating reagent in reactions with fluorene, indene, C_6F_5H, Ph_3CH and thiophene (6,7). Phenylcalcium iodide also metalates terminal acetylenes in diethyl ether medium (8):

$$RC{\equiv}CH + PhCaI \xrightarrow{Et_2O} RC{\equiv}CCaI + C_6H_6$$

(R = Ph, n-Pr, n-Bu, $EtOCH_2$,
i-BuCMe(O-2-pyranyl)

The products were isolated as pure, crystalline solids which were insoluble in common aprotic solvents and were stable to 250°.

Reactions of organocalcium compounds with organic substrates have been studied by several groups. Addition of preformed RCaI to C=O bonds (PhCH=O, CO_2) was reported (4), and of Ph_2Ca to $Ph_2C{=}O$ and CO_2 (1). The action of CH_3CaI on acetone resulted in enolization and formation of mesityl oxide in 95% yield (4). Aldehydes and other enolizable ketones reacted similarly.

The products obtained by reaction of methylcalcium iodide in THF (which consisted of a solution and a solid phase) with diisopropyl ketone consisted of the expected addition product (29%) and the reduction product, i-Pr_2CHOH, (71%). Further experiments showed that it was the CH_3CaI which was in solution which added to the C=O bond and that the insoluble reagent caused the observed reduction (9). The reaction of organocalcium iodides with benzhydrol and substituted benzhydrols gave $Ar_2CHOCaI$ species (5). These reagents reacted with various formate and oxalate esters to give as products the ethers, $(Ar_2CH)_2O$.

Further additions of organocalcium iodides to enynes have been reported:

$$CH_2{=}CMe{-}C{\equiv}CCH{=}CH_2 + RCaI \longrightarrow \xrightarrow{H_2O} CH_2{=}CMe{-}CH{=}C{=}CCH_2R$$

(R = Et, n-Pr, n-Bu, i-Bu, n-C_5H_{11},
Ph, m-MeC_6H_4) (ref. 10)

$$CH_2{=}CHC{\equiv}CGeEt_3 + RCaI \longrightarrow \xrightarrow{H_2O} RCH_2CH{=}C{=}CHGeEt_3 + RCH_2CH_2C{\equiv}CGeEt_3$$

(ref. 11) (1:1)

$$CH_2{=}CHCH{\equiv}CCH{=}CH_2 + RCaI \longrightarrow \xrightarrow{H_2O} CH_2{=}CHCH{=}C{=}CHCH_2R$$

(ref. 12)

(R = Et, n-Pr, n-Bu,
i-Bu)

Diethylbarium reacts similarly (13):

$$CH_2{=}CHC{\equiv}CR + Et_2Ba \longrightarrow \xrightarrow{H_2O} EtCH_2CH{=}C{=}CHR$$

(R = Me, Et, n-Pr, n-Bu, t-Bu)

The alkaline earth metals undergo electron transfer to suitable arylolefins and aromatic compounds to give radical anion and dianion species. These can initiate vinyl polymerization and such systems have received continued study. We note the following reports in this area: preparation of the "living" oligomer of α-methylstyrene in the presence of barium (14); copolymerization of styrene and methyl methacrylate in the presence of calcium (influence of benzoquinone) (15); polybutadienyl-barium (16); polymerization of methyl methacrylate and copolymerization of this monomer with styrene initiated by calcium, strontium and barium (17, 18); copolymerization of butadiene, isoprene and styrene initiated by the alkaline earth metals (19); barium-initiated anionic polymerization (20); relative reactivity of alkaline earth metals in electron transfer, anionic polymerization initiation and propagation reactions (21). Other studies have been devoted to electron transfer reactions involving alkaline earth metals and polynuclear aromatic hydrocarbons (22, 23) and to species present in a THF solution of strontium fluorenide (24).

Organocalcium intermediates may be involved in the defluorination of perfluorinated compounds by calcium atoms, e.g., a C_6F_5-Ca intermediate in the case of hexafluorobenzene (25).

REFERENCES

1. M. A. Zemlyanichenko, N. I. Sheverdina, V. A. Chernoplekova and K. A. Kocheshkov, Zh. Obshch. Khim., 42 (1972) 841
2. P. West and M. C. Woodville, Ger. Offen. 2,132,955 (1972); Chem. Abstr., 76 (1972) 99814x
3. M. Chastrette and R. Gauthier, C. R. Acad. Sci. Paris, Ser. C., 274 (1972) 1101
4. A. V. Bogatskii, T. K. Chumachenko, A. E. Kozhukhova and M. V. Grenaderova, Zh. Obshch. Khim., 42 (1972) 403
5. I. I. Lapkin, M. N. Rybakova, M. I. Belonovich and L. V. Galishevskaya, Zh. Obshch. Khim., 42 (1972) 1381
6. K. A. Kocheshkov, M. A. Zemlyanichenko and N. I. Sheverdina, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 2617

7. M. A. Zemlyanichenko, N. I. Sheverdina and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, 202 (1972) 595

8. L. L. Ivanov, V. P. Nepochatykh and N. A. Smyslova, Zh. Org. Khim., 7 (1971) 2623

9. M. Chastrette and R. Gauthier, C. R. Acad. Sci. Paris, Ser. C., 274 (1972) 2013

10. L. N. Cherkasov, Zh. Org. Khim., 7 (1971) 1319

11. L. N. Cherkasov, Zh. Obshch. Khim., 42 (1972) 1528

12. L. N. Cherkasov, Zh. Vses. Khim. Obshchest., 17 (1972) 111; Chem. Abstr., 76 (1972) 99010g

13. L. N. Cherkasov, G. I. Pismennaya, K. V. Balyan and A. A. Petrov, Zh. Org. Khim., 7 (1971) 2437

14. L. Christmann-Lamande, R. Nuffer and B. Francois, C. R. Acad. Sci. Paris, Ser. C, 274 (1972) 1145

15. C. Mathis and B. Francois, C. R. Acad. Sci. Paris, Ser. C., 274 (1972) 1263

16. R. Nuffer, L. Christmann-Lamande and B. Francois, C. R. Acad. Sci. Paris, Ser. C, 274 (1972) 1336

17. C. Mathis and B. Francois, Makromol. Chem., 156 (1972) 7

18. C. Mathis and B. Francois, Makromol. Chem., 156 (1972) 17

19. P. Maleki and B. Francois, Makromol. Chem., 156 (1972) 31

20. A. A. Arest-Yakubovich and L. N. Moskalenko, Vysokomol. Soedin., 13A (1971) 1242

21. L. N. Moskalenko and A. A. Arest-Yakubovich, Int. Symp. Macromol. Chem., Helsinki, Vol. 1 (1972) 327

22. L. N. Moskalenko and A. A. Arest-Yakubovich, Dokl. Akad. Nauk SSSR, 196 (1971) 142

23. L. N Moskalenko and A. A. Arest-Yakubovich, Dokl. Akad. Nauk SSSR, 206 (1972) 1124

24. T. E. Hogen-Esch and J. Smid, J. Amer. Chem. Soc., 94 (1972) 9240

25. K. J. Klabunde, J. Y. F. Low and M. S. Key, J. Fluorine Chem., 2 (1972) 207