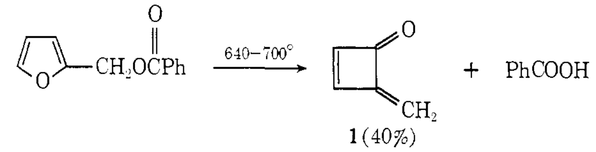
Formation of Methylenecyclobutenone from the Pyrolysis of Furfuryl Benzoate

Sir:

We wish to report that the low pressure (*ca.* 10^{-4} Torr) gas-phase pyrolysis[1] of furfuryl benzoate[2] gives a substantial yield of methylenecyclobutenone (**1**), the parent of a relatively uncommon system.[4]

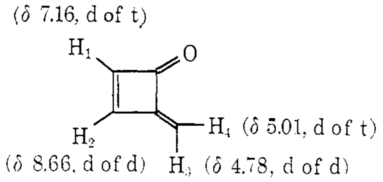


1 (40%)

Methylenecyclobutenone is easily separated from the benzoic acid since the benzoic acid crystallizes at the top of the trap, which is cooled with liquid nitrogen, and **1** condenses at the bottom of the trap. If the trap is warmed before solvent is added, the liquid phase, which is largely **1**, polymerizes to a plastic-like material. This is the same behavior that was noted for neat isopropylidenecyclobutenone (**2**).[4] However, if chloroform or ethyl acetate is added to the trap before warming, a solution of **1** is obtained which is stable enough to handle at room temperature and is stable for weeks when kept at *ca.* −10°. Nmr analyses of these solutions show reasonably pure **1** with very small amounts of benzene, starting ester, and other minor products.

The structure of **1** is based on its ir and nmr spectra and its conversion to 2-methylcyclobutanone by catalytic hydrogenation. The ir spectrum ($CDCl_3$) of **1** shows a strong carbonyl absorption at 1783 cm^{-1} which agrees very well with that reported for cyclobutenone (**3**), 1790 cm^{-1},[5] and cyclobutanone, 1780 cm^{-1},[6] but is somewhat higher than that reported for **2**, 1740 cm^{-1} (neat),[4] and 2-methylenecyclobutanone (**4**), 1765 cm^{-1}.[7] The ir spectrum of **1** also contains strong bands at 1688 (C═C) and 823 ($C{=}CH_2$) cm^{-1}.

The nmr spectrum (EtOAc) of **1** consists of four multiplets of equal intensity. Coupling constants were determined by expansion of each multiplet ($J_{12} = 2.75$, $J_{13} = J_{14} = 0.7$, $J_{23} = 0.0$, $J_{24} = 0.7$, $J_{34} = 1.35$ Hz) and the nmr data are summarized as follows



The chemical shifts of H_1 and H_2 are similar to those of the corresponding protons of **2**, δ 6.82 and 8.78, respectively,[4] and **3**, δ 6.7 and 8.35, respectively.[5] Moreover, the coupling constant between these two protons for **1** is very close to those reported for **2**, 3.0 Hz,[4] and **3**, 2.5 Hz.[5] The chemical shifts of H_3 and H_4 are very similar to those reported for **4**, δ 5.11 and 5.67.[7] The lower field signal was assigned to H_4 since it should be more deshielded by the carbonyl group as it is closer to it.

A quantity of 2.0 mmol of **1** in ethanol–ethyl acetate was hydrogenated using palladium/carbon as the catalyst. After 4.3 mmol of hydrogen was taken up, the reduction slowed down considerably. The ir and nmr spectra of the hydrogenation product, which was purified by glpc, matched exactly those reported for 2-methylcyclobutanone.[8]

Pyrolyses of 160-mg samples of furfuryl benzoate were carried out with the column temperature at 640–700°, head temperature at 30–40°, and pressure at *ca.* 10^{-4} Torr. The pyrolyses took 2–3 hr. After the pyrolysis, a known amount of an internal standard, 1,2-dibromoethane, and chloroform-*d* were added to the trap and the yield of **1** was determined by nmr analysis. For three runs, 38–40% **1**, 3% benzene, 1% starting ester, and traces of other materials were obtained.

The mechanism of the formation of **1** and extension of this reaction to substituted furfuryl esters are under active investigation.

(1) Pyrolyses were carried out as described by W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, **36**, 3575 (1971).

(2) This ester was synthesized from furfuryl alcohol and benzoyl chloride: nmr (neat) δ 8.82–7.83 (m, 2, *o*-phenyl), 7.38 (m, 1, H_5), 7.33–7.00 (m, 3), 6.44 (br d, $J = 3.2$ Hz, H_3), 6.26 (d of d, $J = 3.2$ Hz, $J' = 1.8$ Hz, H_4), and 5.30 (s, 2); ir (CCl_4) 1720 (vs), 1265 (vs), 1250 (vs), 1105 (s), and 1090 (s) cm^{-1}; bp 117–119° (1.5 mm) (lit.[3] bp 275–285° (760 mm)).

(3) L. von Wissel and B. Tollens, *Justus Liebigs Ann. Chem.*, **272,** 301 (1892).

(4) R. C. De Selms and F. Delay, *J. Amer. Chem. Soc.*, **95**, 274 (1973), and references cited therein.

(5) J. B. Sieja, *ibid.*, **93**, 2481 (1971).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 42.

(7) M. Mühlstädt and H. Meinhold, *J. Prakt. Chem.*, 37, 162 (1968).

(8) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

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Received May 18, 1973

Lewis Acidic Metal Alkyl–Transition Metal Complex Interactions. I. Niobium and Tantalum Hydrides

Sir:

Lewis acidic metal alkyls, especially those of aluminum, are widely used on an empirical basis as "promoters" of reactions catalyzed by transition metal complexes, but generally little is known about the interactions involved.[1] In this article we characterize in detail the reactions of dicyclopentadienylniobium and -tantalum hydrides with alkyls of aluminum, gallium, zinc, cadmium, and hafnium.[2,3] The products are either simple Lewis acid–base adducts or compounds formed by alkane elimination from these adducts. Compounds isolated in a pure crystalline form are presented in Table I.

Triethylaluminum reacts rapidly with cyclopentadienylniobium and -tantalum hydrides in benzene solu-

(1) (a) The Lewis basicity of transition metal complexes is reviewed by J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev. A*, **4**, 479 (1969), and by D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970); (b) reactions of metal carbonyls with Lewis acids are reviewed by D. F. Shriver and A. Alich, *Coord. Chem. Rev.*, **8**, 15 (1972).

(2) Other well-characterized hydride reactions are those of Cp_2WH_2,[3a] Cp_2ReH,[3a] Cp_2ZrH_2,[3b] and $CpMoH(CO)_2PR_3$[3c] with group IIIa alkyls.

(3) (a) H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **1**, 125 (1965); (b) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **43**, C29 (1972); (c) W. R. Kroll and G. B. McVicker, *Chem. Commun.*, 591 (1971).