TABLE 2

METHOXY(ACETYLACETONATO)ALKYLTIN HALIDES: $[(CH_3O)(C_5H_7O_2)SnYX]_2$

| Y | X | M.p. (°C) | % C | | % H | | % X | |
|---|---|---|---|---|---|---|---|---|
| | | | Found | Calcd. | Found | Calcd. | Found | Calcd. |
| $CH_3$ | Cl | 188 (dec.) | 28.17 | 28.09 | 4.30 | 4.38 | 11.97 | 11.85 |
| $CH_3$ | Br | 187 (dec.) | 24.48 | 24.46 | 3.81 | 3.81 | 23.20 | 23.25 |
| $C_2H_5$ | Br | 175–6 (dec.) | 26.99 | 26.86 | 4.17 | 4.23 | 22.25 | 22.34 |
| n-$C_4H_9$ | Cl | 99–100 | 35.15 | 35.18 | 5.67 | 5.61 | 10.51 | 10.39 |

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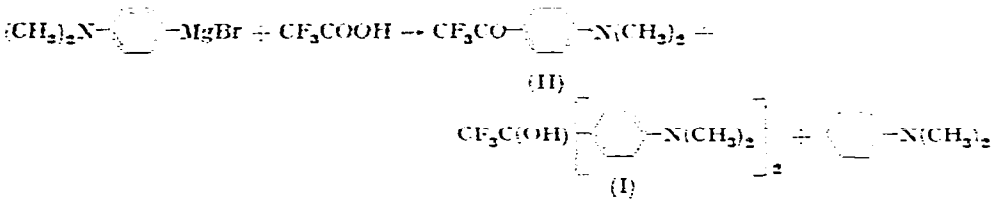
## Reaction of *p*-(dimethylamino)bromobenzene with "activated" magnesium

It has been shown by Ehrlich and Sachs[1] that *p*-(dimethylamino)bromobenzene could react with magnesium powder if initially activated by bromoethane (entrainment method). Subsequently, this method for the preparation of *p*-(dimethylamino)phenylmagnesium bromide was employed by several other investigators[2–6]. As a result of the unimpressive yields of this Grignard reagent, however, the lithium reagent is usually preferred. Recently, Owen[7] described the preparation of this Grignard reagent in tetrahydrofuran (THF) after initiation with ethyl iodide or iodine.

In regard to another problem in this laboratory, a procedure has been discovered for the activation of magnesium turnings such that the resultant "activated" magnesium can be caused to react completely with *p*-(dimethylamino)bromobenzene in refluxing tetrahydrofuran *without* the aid of an initiation agent such as iodine or an entrainment reagent such as a haloalkane. The facile activation procedure involves the one day (or longer) room temperature mechanical stirring of magnesium turnings in a nitrogen atmosphere (to prevent oxide formation of the resultant grey-black, finely divided magnesium). Addition of *p*-(dimethylamino)bromobenzene in THF to such magnesium with gentle reflux of the THF results in a black solution with complete or nearly complete reaction of the magnesium.

Addition of ethyl trifluoroacetate to this Grignard reagent afforded (trifluoromethyl)bis[*p*-(dimethylamino)phenyl]-carbinol (I) (62 % yield). All attempts failed in control experiments to cause conventional magnesium turnings to react with *p*-(dimethylamino)bromobenzene in refluxing THF (for up to two days) under otherwise identical experimental conditions. An attempt to activate the magnesium by another method (aluminum isopropoxide)[8] with hoped for subsequent reaction with this bromide failed.

Addition of trifluoroacetic acid to *p*-(dimethylamino)phenylmagnesium bromide gave on work-up *p*-(dimethylamino)-α,α,α-trifluoroacetophenone (II) (52 % yield) and in smaller quantities carbinol (I) and *N*,*N*-dimethylaniline as illustrated:



Studies now in progress involve the hoped for reaction of "activated" magnesium with other "unreactive" halides or halides known to form Grignard reagents only by a method such as entrainment or transmetallation.

*Experimental*

Melting points are uncorrected. They were determined with a Thomas–Hoover capillary melting point apparatus. Boiling points are uncorrected. Infrared spectra were taken with a Perkin–Elmer Model 21 spectrophotometer. Analyses were performed by the Microanalytical Section of these laboratories.

*Activation of magnesium.* Magnesium turnings (Mallinckrodt) or magnesium chips (Metal and Thermit Corporation), contained in a flask with a teflon-paddle mechanical stirrer, reflux condenser, pressure-equalizing addition funnel, and purified nitrogen purging system, were stirred for one day under nitrogen. After this time, the magnesium was finely divided and developed a grey to grey-black color.

*p-(Dimethylamino)phenylmagnesium bromide.* To 1.22 g (0.05 g atom) of "activated" magnesium was added dropwise over *ca.* 0.5 h with gentle heat to effect reflux 10 g (0.05 mole) of *p*-(dimethylamino)bromobenzene (Eastman-recrystallized from methanol until *white*, m.p. 53–54° and stored in a Drierite-containing desiccator until used) in 75 ml of THF (purified by distillation from and storage over calcium hydride and filtered before use). The product was heated under reflux for three hours with efficient stirring. The reagent was used as described below.

*(Trifluoromethyl)bis[p-(dimethylamino)phenyl]carbinol.* To the above Grignard reagent (at reflux temperature) was added dropwise over ten minutes 7.15 ml (8.5 g, 0.06 mole) of ethyl trifluoroacetate (freshly distilled before use, Peninsular Chemresearch, Inc.) in 10 ml of THF. During this addition, the solution's color changed from black to rose. The mixture was refluxed for 1 h, poured onto ice, and extracted several times with ether. The separated ethereal solution was dried (anhydrous magnesium sulfate), filtered, and the filtrate was distilled (steam bath) to remove ether. The colored residue was purified by steam distillation to give a small amount of

faint-yellow, steam-volatile solid [subsequently identified by infrared spectroscopy and mixture melting point determination as compound (II)] and a water-insoluble, non-steam-volatile product. The latter was collected by filtration and air-dried (8.9 g crude). It was recrystallized from cyclohexane to give 5.2 g [62 % yield, based on *p*-(dimethylamino)bromobenzene] of pure compound (I), m.p. 162–163°. The melting point was not depressed on admixture of this sample with the chromatographed and recrystallized product obtained by the addition of trifluoroacetic acid to *p*-(dimethylamino)phenylmagnesium bromide (see below). (Found: C, 63.9; H, 6.5; N, 8.2: $C_{18}H_{21}F_3N_2O$ calcd.: C, 63.9; H, 6.3; N, 8.3 %.)

*Addition of trifluoroacetic acid to p-(dimethylamino)phenylmagnesium bromide.* The Grignard reagent was prepared as described above by the 0.5 h dropwise addition of 15 g (0.075 mole) of *p*-(dimethylamino)bromobenzene in 65 ml of THF onto 1.82 g (0.075 g atom) of "activated" magnesium. It was heated under reflux thereafter for 1 h and allowed to cool to room temperature. To the black solution was added dropwise over 0.5 h 1.75 ml (2.6 g. 0.025 mole) of trifluoroacetic acid (F C 21–3 M Company) in 25 ml of anhydrous ether. The resulting product was stirred for 1 h thereafter and poured onto ice. The mixture was extracted with ether and the separated ethereal extract was dried (anhydrous magnesium sulfate), filtered, and the filtrate was distilled to remove ether. The residue was distilled then under reduced pressure to give as a first fraction 3.76 g of nearly colorless liquid (b.p. 67–74°/10 mm, $n_D^{23}$ 1.5583) which was identified by its infrared spectrum and refractive index as dimethylaniline, $n_D^{20}$ 1.5582. A second fraction (3.68 g, b.p. 121–124°/1.25 mm) crystallized in the receiver. It was recrystallized from hexane to afford 2.78 g (52 %) of ketone (II) as faint yellow platelets, m.p. 74–75°, lit.[9] m.p. 74.5–75.5°. The 2–3 g residue of this distillation was taken up in 75 ml of benzene and chromatographed on a column (90 × 25 mm) of neutral alumina (California Corporation for Biochemical Research), activity II. Elution with three 50-ml portions of benzene afforded an additional 55 mg of ketone (II) (m.p. 74–75°). Continued elution with benzene (240 ml) and 50 % ether/benzene (300 ml) afforded after recrystallization from cyclohexane 650 mg of compound (I), m.p. 163–164°, identified by mixture melting point and superimposable infrared spectra.

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