

rather than acylmetal carbonyls. The latter are to be expected on the basis of mechanistic studies of carbon monoxide insertion and decarbonylation reactions of manganese carbonyl systems.<sup>2,7,8</sup> The attachment of the alkyl group to  $\text{SO}_2$  in  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{R}$  may result from an initial formation of acyl sulfur dioxide complexes,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{COR})\text{SO}_2$ , followed by a rapid migration of R onto the  $\text{SO}_2$  ligand. However an alternative possibility—direct attack of  $\text{SO}_2$  on iron, accompanied by a transfer of R—cannot be ruled out at present. Both of these mechanisms are consistent with a relatively slow insertion reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$ , since in each case migration of a bulky phenyl group would be involved.

Work continues on the synthesis of the analogous sulfonyl complexes of other transition metals and on the mechanism of sulfur dioxide insertion.

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### Gaseous Alane and Dialane

Sir:

The only trivalent hydride of aluminum that has hitherto been reported in the literature is the crystalline  $(\text{AlH}_3)_x$ .<sup>1</sup> We now wish to describe the conditions under which the gaseous hydrides  $\text{AlH}_3$  and  $\text{Al}_2\text{H}_6$  can be observed. Because of the electron-deficient character of monomeric  $\text{AlH}_3$ , it is predictable that this molecule would readily polymerize at normal pressures, as would also the dimeric  $\text{Al}_2\text{H}_6$  in which the aluminum atoms have coordination numbers of four rather than six. Accordingly, the molecules  $\text{AlH}_3$  and  $\text{Al}_2\text{H}_6$  can only be sought at very low pressures where the polymerization rates are minimized. The technique selected for this study was to follow, in a continuous fashion by time-of-flight mass spectrometry, the gaseous products formed by slow evaporation of aluminum from a hot tungsten filament into hydrogen at low pressure. Siegel<sup>2</sup> had previously shown that the evaporation of aluminum into a hydrogen pressure of about 1 mm. can result in the trapping out of a solid aluminum hydride at  $-195^\circ$ . However, the latter study was carried out in a static system, while the present investigation is with a flow system at even lower hydrogen pressures and no cold wall. The present authors<sup>3</sup> have demonstrated previously the utility of time of flight mass spectrometry in studying gaseous hydrides formed at low pressures; Fehlner and Koski<sup>4</sup> have observed the analogous  $\text{BH}_3$  molecule directly by mass spectrometry, despite the fact that it is normally present in very small amounts in equilibrium with  $\text{B}_2\text{H}_6$ .

Our general method was as follows. In a glass high vacuum system, purified hydrogen was continuously flown past a tungsten wire heating element charged with an aluminum wire which had been melted to a liquid droplet. The pressure at the heating element, as measured by a McLeod gauge, was maintained at 0.3 mm. by a pumping system. During the course of a

run, the temperature of the aluminum charge, as measured by an optical pyrometer, was raised gradually in small increments. It was necessary to have the optical pyrometer at a window offset several inches from the reactor wall since unchanged aluminum deposited rapidly on the wall. Downstream of the aluminum droplet, the flow system divided into paths leading to the pump and to the gold leak of the fast reaction inlet system of a Bendix time-of-flight mass spectrometer. Commencing with the first heating of the aluminum charge, continuous recordings of the mass spectra were obtained as the temperature was increased, a new spectrum being obtained every 3 to 5 min., with an ionizing potential of 70 e.v. The geometry and flow rate were such that the residence time, from introduction of aluminum vapor to mass spectrometer sampling, was 39 msec., with aluminum evaporation rates in the temperature range  $1170\text{--}1250^\circ$  of 0.09 to 0.12 mg./sec.

Numerous mass spectra taken at aluminum droplet temperatures up to  $1030^\circ$  gave no evidence of hydride formation. However, a small mass peak at  $m/e = 30$  was observed when the droplet temperature reached approximately  $1090^\circ$ . That this could be attributed to  $\text{AlH}_3^+$  was verified by substitution of deuterium for hydrogen, whereupon we observed the expected shift to  $m/e = 33$ . The intensity of the  $\text{AlH}_3^+$  peak remained constant over a number of mass spectra. A mass peak for  $\text{Al}_2\text{H}_6^+$  was not observed in these spectra. When the temperature of the aluminum droplet was increased to about  $1170^\circ$ , a mass peak at  $m/e = 60$  was noted with hydrogen. That this was due to  $\text{Al}_2\text{H}_6^+$  was demonstrated by a shift to  $m/e = 66$  when deuterium was substituted for hydrogen. When  $\text{Al}_2\text{H}_6^+$  was first observed, the ratio of ion intensities,  $\text{Al}_2\text{H}_6^+/\text{AlH}_3^+$ , was only 0.1 to 0.5. Upon further heating of the aluminum droplet, this ratio progressively increased, ultimately reaching 11 before the aluminum droplet was depleted. The ratio of ion intensities  $\text{AlH}_3^+/\text{H}_2^+$  was 0.0017 for most spectra, while the  $\text{Al}_2\text{H}_6^+/\text{H}_2^+$  ratio rose to a maximum of 0.019.

Since  $\text{AlH}_3^+$  was observed at lower aluminum vapor pressures than was the case for  $\text{Al}_2\text{H}_6^+$ , and since the ratio  $\text{Al}_2\text{H}_6^+/\text{AlH}_3^+$  progressively increased with temperature, it is clear that these ions are indicative of the neutral species  $\text{AlH}_3$  and  $\text{Al}_2\text{H}_6$ . From the data, it is also apparent that monomeric  $\text{AlH}_3$  is the first hydride to be formed at the lowest pressures of aluminum. However, when the latter become more appreciable, the dimerization  $2\text{AlH}_3 \rightarrow \text{Al}_2\text{H}_6$  becomes predominant. Mass spectra at mass numbers up to 120 were also taken, but higher polymers were not observed under the conditions described.

From equilibrium vapor pressure data on aluminum<sup>5</sup> and the observed aluminum droplet temperatures corresponding to hydride formation, the initial concentrations of Al vapor in  $\text{H}_2$  were  $\sim 0.43\%$  for  $\text{AlH}_3$  formation and  $\sim 1.7\%$  for  $\text{Al}_2\text{H}_6$  formation at minimum intensity. Without knowledge of the ionization cross section for  $\text{Al}_2\text{H}_6$ , its pressure cannot be computed exactly from the relative abundances of  $\text{Al}_2\text{H}_6^+/\text{H}_2^+$ . However, by assigning a maximum ratio of 100 to the

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relative cross sections of these molecules, we obtain a crude lower limit of  $6 \times 10^{-5}$  mm. for the  $\text{Al}_2\text{H}_6$  pressure at maximum intensity. That the actual pressure was higher than this value was demonstrated by measuring both the rates of aluminum evaporation from the aluminum droplet and deposition of aluminum on the wall of the apparatus under conditions where hydrides were observed mass spectrometrically. The differences were attributed to hydride formation since the aluminum deposition occurred only in the immediate vicinity of the droplet. From these data and aluminum vapor pressure data, the calculated hydride pressures ranged from  $10^{-4}$  to  $10^{-3}$  mm.

The observed ready dimerization of  $\text{AlH}_3$  is entirely expected since the latter can be assumed to be  $sp^2$  hybridized with only three filled orbitals. Dimerization to a structure similar to  $\text{B}_2\text{H}_6$ <sup>6</sup> would involve the formation of two hydrogen bridge bonds with an increase in coordination number of Al from 3 to 4.  $\text{AlH}_3$  would then be expected to be no more stable than  $\text{BH}_3$ , relative to dimerization.

It was not possible to sustain aluminum droplet temperatures much in excess of  $1300^\circ$  with the apparatus described above. A more elaborate evaporator is under construction and will be used to determine whether higher gaseous alanes can be prepared at considerably higher aluminum vapor pressures.

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### Aromatic Alkylation *via* Diazotization

Sir:

We have been able to detect the presence of cymene in the diazotization of isopropylamine by butyl nitrite and an equivalent amount of a carboxylic acid dissolved in excess toluene. No previous report of alkylation by this procedure has been found in the literature although a similar method has been used for arylation.<sup>1</sup>

Acetic acid (0.02 mole) was added to toluene (3 ml.) in a test tube containing a clay boiling chip. A mixture of isopropylamine (0.02 mole) and butyl nitrite (0.02 mole) in 3 ml. of toluene was added in increments of 1 ml. over a period of 2 hr. Occasional warming was performed to facilitate gas evolution. The reaction mixture was allowed to stand overnight, refluxed with 25 ml. of 15% aqueous sodium hydroxide, rinsed with water in a separatory funnel, and finally shaken twice with two separate portions of cold, concentrated sulfuric acid. The hydrocarbon layer remaining was washed with water and dried with calcium chloride. Analysis was carried out by means of g.l.c., thermal conductivity detector, 60 ml./min. flow rate of helium, 50- $\mu$ l. sample at attenuation of 2; 5% Bentone 34, 0.5% XF 1150 on Diatoport S: *p*-cymene retention time = 8 min. and *o*- and *m*-cymene = 9.5 min.; 5% polyphenyl ether on Anachrome P, 60-70 mesh: *p*- and *m*-cymene = 10.5 min. and *o*-cymene =

11.5 min. From the first column, the per cent *p*-cymene was obtained, from the second column, the per cent *o*-cymene; the per cent *m*-cymene was obtained by difference.

The total yield of cymenes, based on isopropylamine, was about 3 to 4%, the major products being propylene and isopropyl acetate. The yield of cymenes was nearly the same over a surprisingly large variety of conditions as indicated by the following changes of standard procedure: (1) substitution of pivalic or mesitoic acid or acetic anhydride for acetic acid; (2) change of reaction temperature from 25 to  $60^\circ$ ; (3) stirring, mechanical or sonic cavitation, or no stirring; (4) tenfold increase in toluene concentration; and (5) increased surface area such as crushed clay plate (nitrogen evolution rate increases but not yield). Decrease in acetic acid concentration causes separation of two phases and lowering of the yield.

In such a nonpolar medium the question arises whether a free-radical or ionic mechanism is applicable. We have answered this question by observing the results of the diazotization of *n*-propylamine in benzene using the same conditions as described. About a 1% yield of hydrocarbon was obtained of which 55% was isopropylbenzene and 45% *n*-propylbenzene. These results are similar to those run previously in which the mechanism is an ionic one without doubt.<sup>2,3</sup> To emphasize the improbability of a free-radical mechanism applying to the above results, we quote that not a single reliable demonstration of a primary to secondary migration of a hydrogen atom ( $\text{H}\cdot$ ) has been observed in free radicals to date.<sup>4</sup>

Although the yield of this reaction is too low to be of synthetic value, it is within a satisfactory range to carry out orientation and competition studies. The orientation in isopropylation of toluene was 40-44% *o*-, 24-25% *m*-, and 32-36% *p*-cymene in four different experiments. The competition results were quite interesting as shown in Table I.

TABLE I  
CYMENE/CUMENE RATIOS<sup>a</sup>

A	B	C
Toluene/benzene molar ratio	Cymene/cumene product ratio <sup>b</sup>	Apparent rate ratio ( $k_{\text{C}_6\text{H}_5\text{CH}_3}/k_{\text{C}_6\text{H}_6}$ ), [B $\times$ 1/A]
0.25	0.25	1.0
1.0	0.93	0.93
2.5	2.0	0.8
4.0	3.15	0.79

<sup>a</sup> Acetic acid (0.02 mole) in 3 ml. of toluene-benzene mixtures treated with isopropylamine (0.02 mole) and butyl nitrite in 3 ml. of the same toluene-benzene mixtures in a test tube containing a clay boiling chip. <sup>b</sup> Determined by comparison of Gaussian curve areas in g.l.c.

Benzene is more reactive than toluene. Benzene is even more reactive than *p*-xylene ( $k_{p\text{-xylene}}/k_{\text{C}_6\text{H}_6}$  ca. 0.6). Only one other alkylation experiment is known where benzene has been found to be more reactive than toluene: the alkylation of aromatic hydrocarbons

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