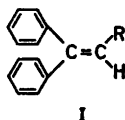


Mass Spectrometry of Some Triarylethylenes

JØRGEN MØLLER and
CARL TH. PEDERSEN

*Physical Laboratory II and Chemical
Laboratory II, University of Copenhagen,
The H. C. Ørsted Institute, Copenhagen,
Denmark*

In connection with a chemical investigation of substituted 1,3-oxathiolan-5-ones we have recorded the mass spectra of some 1,1-diphenyl-2-arylethylenes (I, R = C₆H₅; C₆D₅; *o*-, *m*- and *p*-BrC₆H₄; *o*-, *m*- and *p*-ClC₆H₄) formed by the pyrolysis of 4,4-diphenyl-2-aryl-1,3-oxathiolan-5-ones.¹



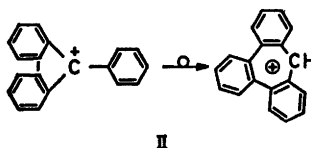
The mass spectra of these compounds are shown in Fig. 1.

The spectra were determined on an Atlas MAT CH 4 mass spectrometer; the ionizing potential was 70 eV, the ionizing current 35 μ A. The samples were introduced through an all-metal inlet system at 150°. The spectra are plotted in terms of relative abundance, with the most intense peak equal to 100%. Only peaks of higher abundance than 2% are recorded, and double charged ions appearing at half mass numbers are omitted.

In parallel to the loss of a methyl radical from the molecular ions of diphenylmethane,^{2,3} stilbene,⁴ and 1,1-diphenylethylene,⁵ a M-15 peak is observed in the mass spectra of triphenylethylene and halogenated triphenylethylenes.

Complete deuterium labelling of the phenyl group in the 2-position of 1,1,2-triphenylethylene shows that approximately half of the eliminated methyl radicals carry away one hydrogen atom from this phenyl group. In the rest of the molecules no hydrogen from this phenyl group is involved in the process. Accordingly, the loss of a methyl radical has to be initiated by two different processes, most probably leading to ions with the identical configuration, II. The two hydrogen atoms

eliminated with the hydrogen atom from the ethylenic CH group are most likely expelled from two rings attached to either the same carbon atom or to each of the ethylenic carbon atoms.



In the halogenated compounds investigated the primary loss of a methyl radical is much decreased owing to the predominant losses of the X, HX and H₂X, (X = Cl or Br). The relative intensities of the M-15 ions decrease successively for *meta*, *para*, and *ortho* halogenated compounds and are smallest for the bromo compounds (*cf.* Table 1).

Table 1. Spectral features of I.

R	M	M-15	M-X	M-X-15
C ₆ H ₅	100	23.9		
<i>o</i> -ClC ₆ H ₄	72	1.6	100	28.2
<i>m</i> -ClC ₆ H ₄	100	5.7	54	17.6
<i>p</i> -ClC ₆ H ₄	100	3.9	48	17.4
<i>o</i> -BrC ₆ H ₄	61	0.4	100	24.2
<i>m</i> -BrC ₆ H ₄	100	4.9	68	34.4
<i>p</i> -BrC ₆ H ₄	100	2.4	66	33.5

Peak heights are expressed in per cents of base peak.

The peak at *m/e* 240 is most probably formed by elimination of a methyl radical from the M-X ion. A metastable peak at *m/e* 238 indicates loss of one hydrogen atom from the ion of mass 240 giving *m/e* 239. These two ions might, however, be formed by loss of CH or CH₂ from the appropriate ions in the mass range 252 to 254. The metastable peaks observed cannot

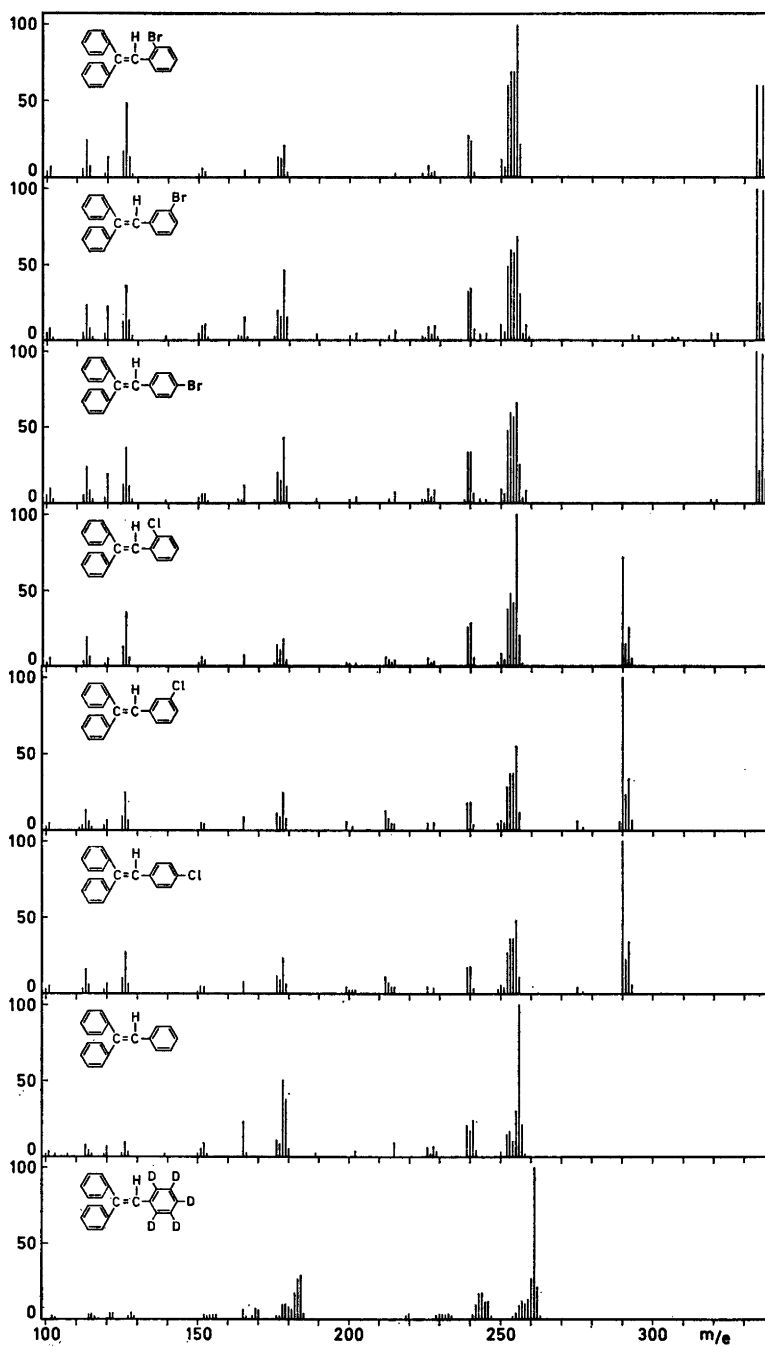


Fig. 1.

be located with sufficient accuracy to exclude these possibilities.

1. Pedersen, C. Th. *Acta Chem. Scand.* **22** (1968) 247.
2. Eland, J. H. D. and Danby, C. J. *J. Chem. Soc.* **1965** 5935.
3. Meyerson, S., Drews, H. and Fields, E. K. *J. Am. Chem. Soc.* **86** (1964) 4964.
4. Johnstone, R. A. W. and Millard, B. J. Z. *Naturforsch.* **21a** (1966) 604.
5. *Catalog of Mass Spectral Data*, American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., Spectrum No. 957.

Received January 24, 1968.

Mechanism of the Grignard Addition Reaction

VI. Product Distribution and Kinetics of the Reaction of Methyl Propionate with Butylmagnesium Bromide in Diethyl Ether

TORKIL HOLM and INGA BLANKHOLM

Department of Organic Chemistry, The Technical University, Lyngby, Denmark

In an earlier study¹ the kinetics of the reaction of methyl acetate with butylmagnesium bromide was investigated by means of a thermographic method. It seemed of interest, however, to follow this type of reaction by more conventional analytical methods. Gaschromatography of cause is the method of choice for determination of low boiling material in ether, but it was found convenient to use methyl propionate as the substrate instead of the acetate.

Quenching of the excess Grignard reagent which must precede the analytical process was found to be a difficult step, and rigorous precautions were necessary to avoid uncontrolled reaction during the work-up procedure. Whereas the thermographic method will handle very fast Grignard reactions (half lives of a few msec) methods

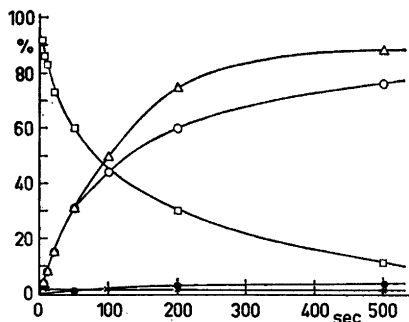


Fig. 1. Relative concentrations (in per cent of 0.050 M) of reaction products at the time indicated in the reaction at 20° of 0.050 M methyl propionate with 0.50 M butylmagnesium bromide in ether solution. Methyl propionate \square , dibutylethylcarbinol \circ , 3-heptanone \times , 3-heptanol \bullet . Also shown is the relative concentration of dibutylethylcarbinol (in per cent of 0.005 M) for the reaction at 20° of 0.0050 M methyl propionate with 0.50 M butylmagnesium bromide \triangle .

requiring quenching must be considered at least a thousand times slower.

Gaschromatographic analyses of the products from the reaction of 0.050 M methyl propionate with 0.500 M butylmagnesium bromide showed the presence of 3-heptanone, 3-heptanol, and dibutylethylcarbinol. Table 1 and Fig. 1 show the concentrations obtained at various times after mixing.

During the reaction the concentrations of ester and tertiary alcohol decrease, respectively increase in a complementary manner showing that no important build up of intermediates is taking place. The heptanol concentration increases in pace with the tertiary alcohol and accounts for approximately 5.5% of the starting material at infinite reaction. The 3-heptanone concentration varies very little during the course of the reaction and accounts for 1.6% of the starting material.

The reaction of 3-heptanone with butylmagnesium bromide was found to lead to very nearly the same concentrations of these three products. It therefore seems reasonable to assume that this ketone occurs as an actual intermediate and undergoes enolization, reduction, and addition in the ratios 1.6:5.5:90.

By means of the thermographic method² the initial rate of reaction of 3-heptanone