

tion of 5.2 g. (0.05 mole) of sodium carbonate in 50 ml. of water. After thirty minutes of refluxing, a yellow liquid product began to separate on the walls of the flask. Refluxing was continued for a total of twelve hours. The aqueous solution was removed by decantation and the yellow residue dissolved in ether. The aqueous layer was extracted with ether and the ethereal solutions combined and dried over magnesium sulfate. The ether was allowed to evaporate at room temperature in a vacuum desiccator, the final traces being removed by cautious evacuation. The viscous liquid material was then yellow-orange in color and was readily soluble in benzene, ether, and methanol, but insoluble in water. The yield was 4.8 g. (57.0%). The nitrogen analysis indicates a D. P. of 8 to 12.

*Anal.* Calcd. for  $C_9H_{16}N_2O$ : C, 64.25; H, 9.59; N, 16.65. Found: C, 64.17; H, 9.85; N, 14.99.

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RECEIVED MAY 25, 1950

similar result was obtained when the induction period was changed by altering the speed of stirring. It is seen that during the induction period the isomerization proceeds to some extent, but the amount of cracking is very small. Isomerization appears to precede cracking and is the predominant reaction during the induction period, after which cracking becomes important. This conclusion is also supported by the following two facts: (1) In the cracked product isoparaffins but no normal paraffin have been found; (2) in the presence of aluminum chloride isoparaffins are cracked more easily than normal paraffins.

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RECEIVED JANUARY 24, 1950

### Raman Spectroscopic Investigation of the Isomerization of *n*-Hexane

BY SAN-ICHIRO MIZUSHIMA, HIDETOSHI OHNO AND TAKEHISA SAKURA

The isomerization of *n*-hexane in the presence of aluminum chloride has been studied. A mixture of 500 cc. of *n*-hexane (Fischer-Tropsch product), 100 g. of aluminum chloride (Takeda's pure sample) and 2 cc. of water was placed in a flask equipped with a reflux condenser and a mechanical stirrer and maintained at a constant temperature of 45°. The purity of the *n*-hexane used was confirmed by its Raman effect.<sup>2,3</sup>

The liquid product of the reaction was separated by fractional distillation into several fractions and the Raman spectrum of each was photographed. The intensity of the Raman lines characteristic of each of the component hydrocarbons allowed an analysis of the reaction product to be made.<sup>3</sup> Several experiments were made with differing speeds of stirring. For one of them (reaction period four hours) Raman analysis gave this result: isobutane 9%, isopentane 7%, 2,2-dimethylbutane 4%, 2,3-dimethylbutane 2%, 2-methyl- and 3-methylpentane 6%, and *n*-hexane 72%.

The isomerization undergoes an induction period during which no apparent change such as the evolution of bubbles can be observed. In one example stopped immediately after this induction period (110 minutes), 5% of *n*-hexane had reacted to yield isobutane (0.2%), isopentane (0.2%), 2,2-dimethylbutane (1%), 2,3-dimethylbutane (1%), and 2-methyl- and 3-methylpentane (2%). The Raman analysis is very useful for the detection of such small changes. A

(1) For previous investigations see Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, 1937, and also Calingaert and Beatty, *THIS JOURNAL*, **68**, 51 (1936).

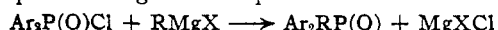
(2) For a description of our Raman apparatus see *s. g.* Mizushima and Morino, *Proc. Ind. Acad. Sci.*, **8**, 315 (1938), Raman Jubilee Volume.

(3) Recent data on the Raman spectra of *n*-hydrocarbons are given in: Mizushima and Shimanouchi, *THIS JOURNAL*, **71**, 1320 (1949).

### The Action of Grignard Reagents on Diaryl Phosphinyl Chlorides<sup>1</sup>

BY D. C. MORRISON

In connection with work on incorporation of radioactive phosphorus into organic molecules, it was found necessary to study the action of Grignard reagents on the chlorides of aromatic phosphinic acids. This reaction has not been examined previously. The product of the reaction is an unsymmetrical alkyldiarylphosphine oxide of the type  $Ar_2RPO$  (where R refers to alkyl and Ar is aryl), and is formed apparently by simple replacement of the halogen atom by an alkyl group according to the equation



The reaction proceeds smoothly to give fair to good yields of the phosphine oxides. The melting points of these compared reasonably well with previous literature values and are recorded in Table I. The phosphinyl chlorides were not isolated as such, but were used as obtained in toluene solution by the action of thionyl chloride on the free acid in this solvent. One of the phosphine oxides which was prepared was not previously described in the literature. This is diphenylbutylphosphine oxide, and for characterization was converted into the nitro derivative.

TABLE I

Compound	M. p., °C., lit.	M. p., °C., uncor. Found	Yield, %
$C_2H_5(C_6H_5)_2PO$	121 <sup>a</sup>	123-124	67.2
<i>i</i> - $C_3H_7(C_6H_5)_2PO$	145-146 <sup>b</sup>	144-146	44.6
<i>i</i> - $C_4H_9(C_6H_5)_2PO$	137.5-138 <sup>b</sup>	132.5-134	75.2
$C_6H_5CH_2(C_6H_5)_2PO$	192-193 <sup>b</sup>	189-190	69.0
$CH_2(p-CH_2-C_6H_4)_2PO$	143 <sup>c</sup>	145.5-146.5	63.8
$C_4H_9(C_6H_5)_2PO$	.....	89.5	68.0
$C_6H_5(NO_2-C_6H_4)_2PO$	.....	124-125.5	68.4

<sup>a</sup> Michaelis and Soden, *Ann.*, **229**, 295 (1885). <sup>b</sup> Arbusov, *J. Russ. Phys.-Chem. Soc.*, **42**, 395 (1910); *C.A.*, **5**, 1397. <sup>c</sup> Michaelis, *Ann.*, **315**, 84 (1901).

(1) The work described in this paper was sponsored by the Atomic Energy Commission. It was supported in part by a grant from the Henry, Laura and Irene B. Derham Fund of the American Cancer Society and the Christine Breon Fund.