

two- to threefold change, however, did not appreciably alter the observed rate constant.

No appreciable polymerization of the butene was observed and the amount of gas distilled from the samples remained fairly constant throughout the runs. Solution appeared to be complete in all cases.

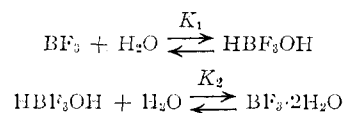
### Discussion

It is difficult to assess the accuracy of the data in Fig. 2. Considerable error in the water concentration is possible, especially at the lower end of the scale due to absorption of the vapor by walls, stop-cock grease, etc., during the transfer from the measuring bulb to the reactor. The fact that the results are reasonably consistent and reproducible suggests that the error from this source is not as great as might be expected, but nevertheless may be important at low water concentrations. The observed rate constants were obtained fairly easily up to a value of about  $0.01 \text{ min.}^{-1}$  but their reliability decreased steadily above that point. The highest rates are essentially estimates as is evident from their scatter.

In spite of their semi-quantitative nature, the results provide some useful information. The sharp peak in the rate with respect to water concentration doubtless accounts for much of the confusion in the literature reports of work in this field, but it must be remembered that the present results are quite possibly characteristic of a limited number of solvents. Furthermore, because of the experi-

mental difficulties involved, and the ease with which the reactions can be poisoned or catalyzed, any results must be regarded with considerable caution until confirmed by independent investigations.

The data shed little light on the detailed mechanism of the catalysis. If toxicity of water at higher concentrations is due to the formation of the dihydrate,  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , which is inactive in catalyzing polymerization, then the rate of isomerization is presumably governed by the equilibria



$K_2$  is probably large, since  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$  is a stable compound, which accounts for the rapid poisoning of the reaction with increasing water concentration. At low water concentrations the rates seem roughly proportional to the total concentrations of water and of boron fluoride, but because of the relationship  $(\text{HBF}_3\text{OH}) = K_1(\text{BF}_3)(\text{H}_2\text{O})$  this cannot be taken as evidence for catalysis by the conjugate acid; a termolecular process involving free water and catalyst is conceivable. More accurate kinetic data together with a knowledge of the constants  $K_1$  and  $K_2$  might help to distinguish between these possibilities but much would depend on the actual values of  $K_1$  and  $K_2$ . An effort is being made to obtain such data.

OTTAWA, CANADA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS AND THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE AMERICAN OIL CO.]

## A Study of the Reaction of Hydrocarbons with Phosphorus Trichloride and Oxygen<sup>1</sup>

BY A. FURMAN ISBELL<sup>2</sup> AND F. T. WADSWORTH<sup>3</sup>

RECEIVED JUNE 28, 1956

A study was made of the factors which influence the yield of alkylphosphonyl dichloride when reaction takes place between a hydrocarbon, phosphorus trichloride and oxygen. Changing the molar ratio of phosphorus trichloride to hydrocarbon changes the yield of alkylphosphonyl dichloride within limits but reaction temperature has virtually no influence. The reaction is very sensitive to impurities. Four new cycloparaffins were employed in the reaction. Nitrocyclohexane, cyclohexene, isopropylbenzene and acetyl chloride failed to react.

The reaction between hydrocarbons, phosphorus trichloride and oxygen, to produce alkylphosphonyl dichlorides, was first described by Clayton and Jensen<sup>4</sup> in 1948. Since that time, they and other workers<sup>4-14</sup> have extended this reaction. How-

ever, the reported yields of the same products have varied widely, experimental conditions have usually been described inadequately and the effects of changes in experimental conditions have not been made clear. We have attempted to make a more thorough study of this reaction.

There is relatively little information in the literature relating simply to the oxidation of phosphorus trichloride to phosphorus oxychloride. Some of this is in disagreement. Certain references<sup>10-19</sup>

(1) Presented at the Minneapolis Meeting of the American Chemical Society, September, 1955.

(2) To whom inquiries should be made: Chemistry Dept., A. & M. College of Texas, College Station, Tex.

(3) American Oil Company.

(4) J. O. Clayton and W. L. Jensen, *THIS JOURNAL*, **70**, 3880 (1948).

(5) W. L. Jensen and J. O. Clayton, U. S. Patent 2,683,168 (1954).

(6) W. L. Jensen and J. O. Clayton, U. S. Patent 2,683,169 (1954).

(7) W. L. Jensen and C. R. Noller, *THIS JOURNAL*, **71**, 2384 (1949).

(8) L. Z. Soborovskii, Yu. M. Zinov'ev and M. A. Englin, *Doklady Akad. Nauk S.S.S.R.*, **67**, 293 (1949).

(9) L. Z. Soborovskii, Yu. M. Zinov'ev and M. A. Englin, *ibid.*, **73**, 333 (1950).

(10) L. Z. Soborovskii and Yu. M. Zinov'ev, *Zhur. Obshchei Khim.*, **24**, 516 (1954).

(11) Y. M. Zinov'ev, I. I. Muler and L. Z. Soborovskii, *ibid.*, **24**, 380 (1954).

(12) P. Lesfauries and P. Rumpf, *Bull. soc. chim. France*, 542 (1950).

(13) R. Graf, *Chem. Ber.*, **85**, 9 (1952).

(14) J. F. Elliott, M. Prober and P. D. George, *Chem. Eng. News*, **33**, 4512 (1955).

(15) R. Abegg, "Handbuch der Anorganischen Chemie," Vol. 3, Sect. 3, Verlag von S. Hirzel, Leipzig, 1907, p. 460.

(16) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., New York, N. Y., 1928, p. 1019.

(17) J. R. Partington, "Textbook of Inorganic Chemistry," The Macmillan and Co., Ltd., London, 1950, p. 378.

would indicate that the oxidation with elemental oxygen is difficult, since there is mention of elevated temperatures, special catalysts and ozone as the oxidizing agent. Other relatively recent references<sup>20-22</sup> point out that with elemental oxygen, reaction takes place readily and under mild conditions, particularly when impurities such as compounds of sulfur, rubber and iron are absent. We found that this reaction takes place rapidly and quantitatively, even at low temperatures, when pure phosphorus trichloride is employed. Trace quantities of the above impurities prevent the reaction completely.

For the reaction involving a hydrocarbon, phosphorus trichloride and oxygen, at least sixteen different catalytic agents<sup>4,12,19</sup> have been tested in an attempt to improve the yield of alkylphosphonyl dichloride. These substances have been reported to produce no effect, to decrease the yield or to prevent the reaction. These reports contain certain disagreements. We found that vanadium pentoxide had no detectable effect on the reaction, whereas Lesfauries and Rumpf<sup>12</sup> stated that it decreased the yield. We can add two additional substances to the list of those that inhibit the reaction completely—iron powder and boron trifluoride.

Employing cyclohexane as the test hydrocarbon, we determined the effects of varying the ratios of reactants and of various reaction temperatures on the yield of cyclohexylphosphonyl dichloride. In going from two moles of phosphorus trichloride per mole of cyclohexane to two moles of cyclohexane per mole of phosphorus trichloride, there was a steady increase in yield of phosphonation product from 20.9 to 29.2%, basis phosphorus trichloride. Surprisingly enough, higher molar ratios of cyclohexane did not increase the yield detectably.

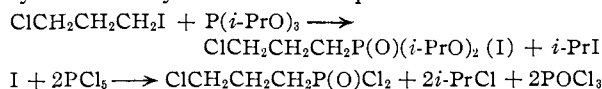
The reaction temperature was varied from  $-100$  to  $+100^\circ$ . Below about  $-40^\circ$  solid phosphorus oxychloride plugged the oxygen inlet line, causing mechanical troubles. The  $+100^\circ$  run was carried out in the vapor phase, with variable flow rates causing difficulties. However, the normal reaction appeared to take place over this entire temperature range and certainly between  $-40$  and  $+70^\circ$  there was no appreciable change in the yield of desired product. The rate of the reaction appeared to be virtually instantaneous, the speed being governed only by the rate at which oxygen could be caused to dissolve in the reaction mixture.

Neither phosphorus oxychloride nor the phosphonation products, when added to the reaction mixture, caused any change in the yield of products. The reaction is not glass surface-catalyzed, as shown by the fact that a normal reaction took place in a reactor of polyethylene.

In a patent<sup>23</sup> air is claimed to be the preferred oxidizing agent and nitrogen dioxide is stated to be

effective also. We found that dry air caused the desired reaction to take place but the reaction rate was very slow, as compared with pure oxygen. When nitrogen dioxide was utilized as the oxidizing agent, an exothermic reaction took place but no expected phosphonation product was isolated by the usual procedure.

Since cyclohexane was the only cycloparaffin which had been employed in this reaction, it appeared desirable to determine the behavior of certain other cycloparaffins. Cyclopentane gave cyclopentylphosphonyl dichloride in 35% yield. Methylcyclopentane and methylcyclohexane gave what were probably isomeric mixtures of phosphonation products in yields of 25-30%. When the reaction was carried out with cyclohexene, an abnormally rapid consumption of oxygen took place, resulting in a large amount of polymeric product and a small amount of distillate boiling over a wide range, which was not characterized. Cyclopropane gave only a 7% yield of phosphonation product, which proved to be  $\gamma$ -chloropropylphosphonyl dichloride. This compound was also synthesized by the reaction sequence



Although Soborovskii, *et al.*,<sup>9</sup> have carried out the oxidative phosphonation reaction on 2,3-dimethylbutane, no product yield was reported. We found this reaction to give much polymeric material along with only 12.5% of crude distillate, which is believed to be a mixture of the two isomeric alkylphosphonyl dichlorides. Additional work on this reaction is in progress.

Three compounds which did not take part in the oxidative phosphonation reaction, were isopropylbenzene, nitrocyclohexane<sup>24</sup> and acetyl chloride.

### Experimental

**General Oxidative Phosphonation Procedure.**—Oxygen was passed through a rotameter (calibrated with a wet test gas meter), through a Drierite drying tube and into the three-necked reaction flask. The flask was also fitted with a stirrer, a Dry Ice condenser and a thermometer. From the condenser, the resulting gases passed through a soda-lime tower and into a wet test gas meter, which metered the unreacted oxygen. All flexible connections were made with Tygon tubing, since rubber tubing inhibits the reaction.

A very critical factor was the degree of oxygen dispersion. Good oxygen dispersion was attained by employing a specially designed stirrer, which was in the form of an inverted, hollow cone, sealed to the bottom of the stirring rod. The largest diameter of the cone was 18 mm. and this tapered to a bottom opening of 8 mm. The height of the cone was 30 mm. At a distance of 10 mm. from the bottom, 8 holes of approximately 0.5 mm. diameter were spaced equally around the circumference. The end of the oxygen inlet line inside the flask was pulled down to a diameter of 1 mm. and directed into the open end of the cone stirrer. When the stirrer was turned at 2,300 r.p.m., the oxygen dispersion was excellent, and the rate of oxygen uptake was rapid. At about half this speed, the reaction time was increased by a factor of three or more.

The hydrocarbon and  $\text{PCl}_3$  were placed in a flask, the stirrer was started and the oxygen flow was adjusted to 4-20 l. per hr. An acetone-Dry Ice-bath was required to maintain the reaction temperature at  $20^\circ$  or below. When the reaction was complete, evolution of heat ceased. The reaction product was distilled at atmospheric pressure until a pot tem-

(24) A sample of this material was kindly supplied by the du Pont Company.

(18) E. Neuman and A. T. Healey, British Patent 465,526 (1937).

(19) Monsanto Chemical Co., British Patent 727,950 (1955).

(20) M. Mudgan and J. Sixt, German Patent 624,884 (1936).

(21) R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 10, The Interscience Encyclopedia, Inc., New York, N. Y., 1953, p. 480.

(22) J. F. Thorpe and M. A. Whiteley, "Thorpe's Dictionary of Applied Chemistry," Vol. IX, Longmans, Green and Co., London, 1949, p. 520.

(23) California Research Corp., British Patent 648,328 (1951).

TABLE I  
 REACTION OF CYCLOHEXANE, PCl<sub>3</sub> AND O<sub>2</sub>

Run	Moles of reagents		O <sub>2</sub> flow rate, l./hr.	Reacn. time, min.	Reacn. temp., °C.	Yield of cyclohexylphosphonyl dichloride,		
	PCl <sub>3</sub>	Cyclohexane				g.	% basis PCl <sub>3</sub>	% basis cyclohexane
1	2	1	3.8	720 <sup>a</sup>	23-48	58.3	14.5	29.0
2 <sup>b</sup>	2	1	4	No reactn.	...	..	..	..
3 <sup>c</sup>	2	1	6-12.2	345	24-67	81.9	20.4	40.8
4 <sup>d</sup>	2	1	12.2	330	31-71	84.7	21.0	42.0
5 <sup>e</sup>	2	0	13.1	300	26.5-73	..	..	..
6 <sup>f</sup>	2	1	13.5	360	100-105	61.0	15.2	30.3
7	2	1	14.1	120 <sup>g</sup>	-20	74.0	18.4	36.8
8 <sup>h</sup>	2	1	14	210	-20	78.5 <sup>i</sup>	19.5	39.0
9	2	1	14	203	-100 to -10 <sup>j</sup>	75.3	18.7	37.4
10	1.25	2.50	7	165	20-25	73.4	29.2	14.6
11 <sup>k</sup>	1	2	7	125	20-25	54.7	27.2	13.6
12 <sup>l</sup>	1.25	2.50	7	167	20-25	59.8 <sup>m</sup>	23.8	11.9
13 <sup>n</sup>	1.25	2.50	7	385 <sup>o</sup>	-20 to -15	50.2 <sup>p</sup>	19.9	10.0
14 <sup>q</sup>	1.25	2.50	.. <sup>p</sup>	125	22-28	0 <sup>r</sup>	0	0
15	1.28	2.56	20 <sup>r</sup>	470 <sup>s</sup>	20-25	70.5	27.4	13.7
16 <sup>t</sup>	1	3.5	12.2	270	24.5-52	42.8	21.2	6.1
17 <sup>u</sup>	1.25	2.50	7	209	20-25	73.7	29.3	14.7
18 <sup>v</sup>	1	3.5	6-9	201	20-25	52.8	26.2	7.5

<sup>a</sup> Very slow reaction, primarily because of slow stirrer speed. <sup>b</sup> To the reaction mixture 1 g. of 40 mesh iron powder was added. <sup>c</sup> Five grams of V<sub>2</sub>O<sub>5</sub> was also added. <sup>d</sup> Duplication of run 1 with much faster stirrer speed (2300 r.p.m.). <sup>e</sup> Run without cyclohexane. Distilled POCl<sub>3</sub> obtained in 91.5% yield. <sup>f</sup> Reaction carried out in continuous reactor with reagents in vapor phase. Only about 68% of the calculated amount of O<sub>2</sub> appeared to have been absorbed. <sup>g</sup> O<sub>2</sub> flow continued for 2 hr. after exothermic reaction ceased, while flask contents warmed slowly to 50°. <sup>h</sup> Reaction carried out in presence of 4.5 g. of BF<sub>3</sub>. No reaction until all BF<sub>3</sub> purged by O<sub>2</sub> flow. <sup>i</sup> Yield calcd. on aliquot sample. <sup>j</sup> Very little reaction until temp. raised to -70°. Had to continue to raise temp. slowly to prevent plugging of O<sub>2</sub> inlet tube with solid POCl<sub>3</sub>. <sup>k</sup> Reaction carried out in presence of 1 mole of POCl<sub>3</sub>. <sup>l</sup> The products of run 11, except the POCl<sub>3</sub>, were added to this reaction mixture. <sup>m</sup> Corrected for the added product from run 11. Even with this correction, the distillation residue (cyclohexyldiphosphonyl tetrachloride) amounted to about 50% more than normal. <sup>n</sup> All parts of the reaction vessel were of polyethylene. <sup>o</sup> No stirrer was used. O<sub>2</sub> dispersion was very poor and reaction was slow. <sup>p</sup> NO<sub>2</sub> was used in place of O<sub>2</sub>. <sup>q</sup> POCl<sub>3</sub> was recovered, but no organophosphorus product was isolated. <sup>r</sup> Air was used instead of pure O<sub>2</sub>. <sup>s</sup> Reaction with air was very slow. After 435 min., pure O<sub>2</sub> (20 l./hr.) was fed for 35 min. to complete reaction. <sup>t</sup> The PCl<sub>3</sub> plus 0.5 mole of cyclohexane was added dropwise to the remaining cyclohexane, while the solution was kept saturated with O<sub>2</sub>. <sup>u</sup> PCl<sub>3</sub> added in 11 portions of approx. 10 ml. each beneath surface of cyclohexane, which was kept saturated with O<sub>2</sub>. <sup>v</sup> PCl<sub>3</sub> added continuously throughout reaction beneath surface of cyclohexane, which was kept saturated with O<sub>2</sub>.

 TABLE II  
 REACTION OF OTHER HYDROCARBONS WITH PCl<sub>3</sub> AND O<sub>2</sub>

Run	Hydrocarbon	Moles of reagents		O <sub>2</sub> flow, l./hr.	Reacn. time, min.	Reacn. temp., °C.	Yield of alkylphosphonyl dichloride	
		PCl <sub>3</sub>	Hydrocarbon				g.	% basis PCl <sub>3</sub>
19	Cyclopentane	1.25	2.50	7-12	130	20-25	82.3	35.2
20	Cyclopropane	2.50	8.07	Variable <sup>a</sup>	220	-35 to -30	36.4	7.4 <sup>b</sup>
21	Methylcyclopentane	2.50	5.00	20	150	20-25	154.2 <sup>c</sup>	30.6
22	Methylcyclohexane	2.20	4.40	20	152	20-25	121.7 <sup>c</sup>	25.6
23	Cumene	1.25	2.50	7	135	20-25	0 <sup>d</sup>	0
24	2,3-Dimethylbutane	2.50	5.00	20	137	20-25	63.7 <sup>e</sup>	12.5
25	Cyclohexene	2.00	2.00	14-27.3	68	15-25	0 <sup>d,f</sup>	0
26	Nitrocyclohexane <sup>g</sup>	2.00	1.00	14	.. <sup>h</sup>	25	0	0
27	Acetyl chloride	1.25	2.50	7	181	20-25	0 <sup>d</sup>	0

<sup>a</sup> To prevent plugging of the O<sub>2</sub> inlet line with solid POCl<sub>3</sub>, the discharge end of the tube was raised above the surface of the liquid reactants and the stirrer was adjusted to spray liquid into the top portion of the flask. The off-gas line was immersed to a depth of 4 in. in Hg to produce a slightly elevated pressure. <sup>b</sup> This product was  $\gamma$ -chloropropylphosphonyl dichloride. <sup>c</sup> Probably a mixture of isomers. <sup>d</sup> In these reactions the PCl<sub>3</sub> was oxidized to POCl<sub>3</sub> but little, if any, alkylphosphonyl dichloride was produced. <sup>e</sup> This product was contaminated with a small amount of oil, not hydrolyzable with water and having a decided camphor-like odor. A very large amount of high boiling residue remained in the distillation flask. It appeared to be largely hydrocarbon in nature. <sup>f</sup> A fraction boiling at 90° (6.5 mm.) to 117° (4.0 mm.) weighed 44.5 g. It was obviously a mixture of materials and was not characterized. There remained in the distilling flask 83.3 g. of brown, viscous, polymeric residue. <sup>g</sup> The freshly distilled material still had a light pink color. <sup>h</sup> After 30 min. no oxygen had been consumed and the temperature had not changed.

perature of 150-160 was reached; the residue was distilled at 2-10 mm. A small amount of high-boiling residue normally remained. This has been shown<sup>7</sup> to be primarily the alkyl-diphosphonyl tetrachloride. The results of experiments with cyclohexane are shown in Table I and the results with other hydrocarbons are shown in Table II. The properties of the new alkylphosphonyl dichlorides are listed in Table III.

**Cyclopentylphosphonic Acid.**—Twenty grams of cyclopentylphosphonyl dichloride was added to an excess of wa-

ter and after the mixture became homogeneous, the water was removed *in vacuo*. The brown, solid residue, which was soluble in water, ether, hot benzene and hot toluene, was recrystallized alternately from benzene and toluene, using activated carbon to remove a colored, oily impurity. After five recrystallizations, the pure acid was obtained in the form of small, white needles, melting at 127.5-128.0°. <sup>25</sup> Titration curves on the various acids prepared in this study

(25) All melting points are corrected.

TABLE III

R Group	PROPERTIES OF ALKYLPHOSPHONYL DICHLORIDES, RPOCl <sub>2</sub>			Chlorine, %			<i>n</i> <sub>D</sub> <sup>20</sup>	<i>d</i> <sub>4</sub> <sup>20</sup>
	°C.	B.p. Mm.	Empirical formula	Found	Calcd.	Calcd.		
Cyclopentyl	98	6.2	C <sub>5</sub> H <sub>9</sub> Cl <sub>2</sub> OP	38.20	38.18	37.92	1.4973	1.3171
γ-Chloropropyl	88	2	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> OP	54.36	54.32	54.43	1.4928	1.4580
Methylcyclopentyl	99	5	C <sub>6</sub> H <sub>11</sub> Cl <sub>2</sub> OP	37.28	37.33	35.27	....	....
Methylcyclohexyl	121.5	7	C <sub>7</sub> H <sub>13</sub> Cl <sub>2</sub> OP	33.04	32.24	33.13	....	....
2,3-Dimethylbutyl	80 95	15 9	C <sub>6</sub> H <sub>13</sub> Cl <sub>2</sub> OP	40.10		34.92	....	....

showed that the first acidic hydrogen could be titrated with an indicator, which changes color in the range pH 4.6–5.6.

*Anal.* Calcd. for C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>P: P, 20.64. Found: P, 20.48, 20.43.

**Diisopropyl γ-Chloropropylphosphonate (I).**—3-Chloro-1-propanol (b.p. 74–76° (28 mm.)) was prepared in a 58.2% yield by the method of Marvel and Calvery.<sup>26</sup> This alcohol was converted into 1-chloro-3-iodopropane (b.p. 72–74° (27 mm.)) in a 60.5% yield by the method of Case.<sup>27</sup> 1-Chloro-3-iodopropane (204.5 g., 1 mole) was heated to reflux under vacuum (29 mm.) and 208 g. (1 mole) of triisopropyl phosphite was added dropwise. After refluxing the mixture for 18 hours to complete the reaction and remove isopropyl iodide, the residue was distilled. There was obtained 174.7 g. (72%) of liquid, b.p. 98–105° (1.5 mm.). Redistillation produced a fraction boiling constantly at 106° (1.8 mm.), *n*<sub>D</sub><sup>20</sup> 1.4395, *d*<sub>4</sub><sup>20</sup> 1.0707.

*Anal.* Calcd. for C<sub>9</sub>H<sub>20</sub>ClO<sub>2</sub>P: P, 12.77; *MRD*, 57.29. Found: P, 13.13, 13.14; *MRD*, 59.67.

**γ-Chloropropylphosphonic Acid.**—A sample of the ester I was refluxed with concentrated HCl and the solution was

(26) C. S. Marvel and H. O. Calvery, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 519.

(27) F. H. Case, *THIS JOURNAL*, **55**, 2929 (1933), reported a 58.3% yield of product boiling at 169–173° at atmospheric pressure.

evaporated to dryness *in vacuo*. The white solid residue was recrystallized from benzene and chloroform, producing white plates, m.p. 106.5–107.0°; lit.<sup>28</sup> 95–97.5°.

*Anal.* Calcd. for C<sub>3</sub>H<sub>5</sub>ClO<sub>2</sub>P: Cl, 22.37; P, 19.54. Found: Cl, 22.18, 22.24; P, 19.52, 19.50.

When the phosphonyl dichloride from cyclopropane was hydrolyzed and the acid purified in the same manner, it appeared to be identical in all respects with the above acid. The m.p. of a mixture of the two samples was 105–106°.

**γ-Chloropropylphosphonyl Dichloride.**—To 144.2 g. (0.593 mole) of I, was added slowly, with cooling, 248 g. (1.185 moles) of phosphorus pentachloride. The mixture was warmed slowly to 100° to cause the last of the phosphorus pentachloride to dissolve. Phosphorus oxychloride was distilled at atmospheric pressure and the high boiling residue was distilled *in vacuo*. The fraction boiling at 88–90° (2 mm.) weighed 76.3 g. (65.8%); analytical fraction, b.p. 88° (2 mm.), *n*<sub>D</sub><sup>20</sup> 1.4960, *d*<sub>4</sub><sup>20</sup> 1.4593.

*Anal.* Calcd. for C<sub>3</sub>H<sub>6</sub>Cl<sub>3</sub>OP: Cl, 54.43; *MRD*, 38.24. Found: Cl, 54.36, 54.32; *MRD*, 39.12.

(28) A. R. Stiles, F. F. Rust and W. E. Vaughan, *ibid.*, **74**, 3282 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

## The Addition of *p*-Thiocresol to Bicyclic Olefins. Quantitative Analysis for Rearrangement Products<sup>1</sup>

BY JEROME A. BERSON AND WILLIAM M. JONES

RECEIVED JUNE 5, 1956

The free radical additions of *p*-thiocresol to *exo-cis*-3,6-endomethylene-Δ<sup>4</sup>-tetrahydrophthalic anhydride and the corresponding dimethyl ester give, as major products, the unrearranged *p*-tolylthioethers. The total absence of rearrangement in the products from the reaction of *p*-thiocresol with the ester is demonstrated by isotope dilution analysis.

Although Wagner-Meerwein rearrangements are a familiar feature of the chemistry of bicyclic cations, analogous structural changes appear to be much less common in the corresponding free radicals. Thus, the bicyclic radicals generated in the decarbonylation of bicyclo[2.2.2]octane-2-carboxaldehyde<sup>2</sup> and in chain additions to camphene,<sup>3</sup> β-pinene<sup>4</sup> and norbornene<sup>5</sup> give, as major products,

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1544.

(2) W. von E. Doering, M. Farber, M. Sprecher and K. B. Wiberg, *THIS JOURNAL*, **74**, 3000 (1952).

(3) G. Dupont, R. Dulou and G. Clement, *Bull. soc. chim.*, **1002** (1951).

(4) (a) G. Dupont, R. Dulou and G. Clement, *Compt. rend.*, **230**, 2027 (1950); (b) *Bull. soc. chim.*, 1115 (1950); (c) 257 (1951); (d) D. M. Olroyd, G. S. Fisher and L. A. Goldblatt, *THIS JOURNAL*, **72**, 2407 (1950); (e) these reactions involve ring-opening.

(5) (a) S. J. Cristol and G. D. Brindell, *THIS JOURNAL*, **76**, 5699 (1954); (b) J. Weinstock Abstracts of Papers, American Chemical Society Meeting, Minneapolis, Minn., Sept. 11–16, 1955, p. 19–O.

unrearranged materials. Nevertheless, since many of these reactions give only moderate yields of identifiable products, it is difficult to decide whether or not rearrangement is really a prohibitively unfavorable process. In the work reported here, we have scrutinized the products derived from a bicyclic radical and have demonstrated, by isotope dilution analysis, that rearranged materials are absent.

The additions of *p*-thiocresol to *exo-cis*-3,6-endomethylene-Δ<sup>4</sup>-tetrahydrophthalic anhydride (I) and to the corresponding dimethyl ester II were investigated. Cristol and Brindell<sup>5a</sup> had already shown that the major product (85% yield) of the addition of *p*-thiocresol to the parent hydrocarbon, norbornene, was not rearranged. We chose to work with the anhydride and ester in the anticipation<sup>6</sup> that a carbonyl group properly situated might stabilize the transition state for rearrange-

(6) J. A. Berson, *THIS JOURNAL*, **76**, 5748 (1954).