have been examined.

The oxygen uptake of the homogenate without substrate was inhibited by rotenone, but it was not inhibited when succinate was added.

When *l*-glutamate was added as substrate, the oxygen uptake of the mitochondrial fraction of brain was seriously inhibited by rotenone.

Dihydro-rotenone and rotenolone-I were effective in depressing *l*-glutamate oxidation, but dehydro-rotenone was ineffective.

These results are the same as those obtained in insects which have been reported previously.

References

1) Ambrose, A. M. and H. B. Haag: Ind. Eng. Chem. **29**, 429 (1937).
2) Braustein, A. E.: Advances in Protein Chemistry **3**, 1 (1947).
3) Fukami, J.: Japan. J. Appl. Zool. **19**, 148 (1955).
4) Fukami, J.: Botyu-Kagaku **21**, 122 (1956).
5) Fukami, J. and C. Tomizawa: Botyu-Kagaku **21**, 128 (1956).
6) Fukami, J. and C. Tomizawa: Botyu-Kagaku **23**, 1 (1958).
7) Haller, H. L., L. D. Goodhue and H. A. Jones: Chemical Review **30**, 33 (1942).
8) Nakatsugawa, T., J. Fukami, C. Tomizawa, and H. Ishikura: Abstract of the annual meeting of Japan. Soc. Appl. Entomol. and Zool., Tokyo (1958).
9) Okamoto, A.: Shinkei Kagaku (Neurochemistry), Igaku Shoin, Tokyo (1952).
10) Shepard, H. H. and F. L. Campbell: J. Econ. Entomol. **25**, 142 (1932).
11) Takagaki, G., S. Hirano, and Y. Tsukada: Arch. Biochem. Biophy. **68**, 196 (1957).
12) Tanaka, I., K. Takeda, and T. Takehana: Abstract of the annual meeting of Japan. Soc. Sericul. Soc., Tokyo (1957).
13) Tukada, U.: Seitai no Kagaku (Medical Science) **5**, 107 (1953).

Addition of Dialkyl Dithiophosphoric Acids or Dialkyl Hydrogen Phosphites to Olefinic Compounds. Studies on Organophosphorus Compounds. IV*. Yuji NAGAE, Tomoo WATANABE and Kazuo OHKUMA (Institute of Agricutural Chemicals, Toa Agricultural Chemicals Co., Ltd.**) Received Oct. 6, 1958. *Botyu-Kagaku*, **23**, 208, 1958.

37. Dialkyl dithiophosphoric acid 及び dialkyl hydrogen phosphite のオレフィン化合物への附加 有機燐化合物の研究 第4報 永江祐治・渡辺智夫・大熊一男（東亜農薬株式会社 農薬研究所） 33. 10. 6 受理

殺虫作用を検討する目的を以て，dialkyl dithiophosphoric acid 及び dialkyl hydrogen phosphite のオレフィン化合物への附加反応について研究した．Dialkyl dithiophosphoric acid はアクリロニトリル (VI)，シクロペンタジェン，ジシクロペンタジェン (X) に附加して夫々対応する dithiophosphate (V, VII, VIII, IX) を与えた．同様の附加反応を dialkyl hydrogen phosphite について試み，VI よりは対応する phosphonate (XI, XII) を得たが，X よりは成績体を得ることができなかった．

Mel'nikov *et al*[1]. prepared many dialkyl dithiophosphoric acid esters by addition of dialkyl dithiophosphoric acids to olefinic compounds. Gar *et al*[2]. evaluated their biological properties, and found that dithiophosphates derived from acrylonitrile or diethyl fumarate were the most effective. Dithiophosphate obtained from diethyl fumarate and dimethyl dithiophosphoric acid, is an excellent insecticide known as the trade name "Malathion"[3,4].

Gar *et al.* tested biological properties of dithiophosphates only against *Calandra oryzae*. It seemed to us to be interesting if dialkyl β-cyanoethyl dithiophosphates, prepared by cyanoethylation of dialkyl dithiophosphoric acids, would have the similar biological properties to those of Malathion, which had low toxicity to mammals and specific effects against aphids, mites and green rice leafhoppers. Hence we prepared some dithiophosphates derived from acrylonitrile, espe-

* Part III: Botyu-Kagaku, **23**, 115 (1958).
** Kozu, Odawara, Kanagawa-ken.

cially dimethyl ester which had never been prepared. We preferred dimethyl ester because of its highest effect against green rice leafhopper in general.

When either cyclopentadiene or dicyclopentadiene was used in place of acrylonitrile as an olefinic compound, the corresponding dithiophosphate was obtained in both cases.

Furthermore, addition reaction of dialkyl hydrogen phosphites to olefinic compounds was studied. When acrylonitrile was used as an olefinic compound, dialkyl β-cyanoethyl phosphonate was obtained. However, in both cases of cyclopentadiene and of dicyclopentadiene, phosphonates could not be obtained.

In the case of dithiophosphates derived from cyclopentadiene or dicyclopentadiene, the positions of carbon atoms to which dithiophosphoryl groups attach, are not yet established.

The results of evaluation of biological properties of these compounds will be reported in elsewhere. In general, the compounds synthesized in this report were inferior to Malathion in their biological effects.

Experimental

Dimethyl dithiophosphoric acid (I). I was prepared according to the procedure reported by Fletcher *et al*[5], who used this compoud as intermediate to dimethyl chlorothiophosphate without isolation. Bp_2 56-57°. Yield : 61%.

On distillation, I decomposed with explosion unless the pressure was sufficiently diminished. Usually it required the pressure of 5 mm Hg or less for a satisfactory distillation.

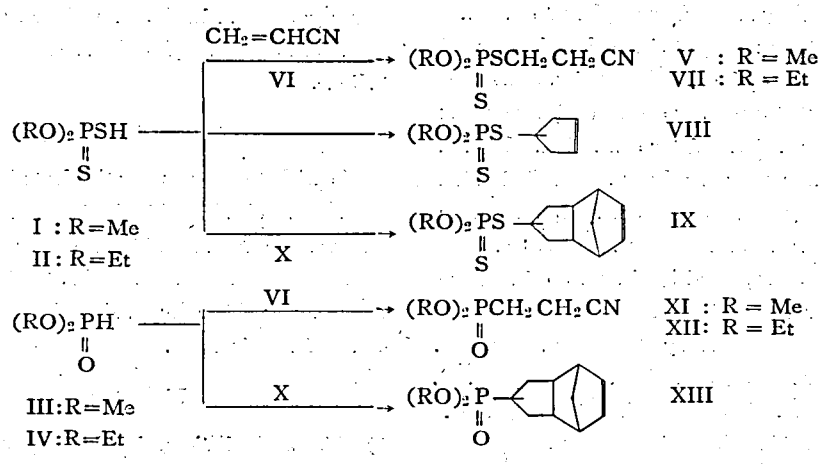
Diethyl dithiophosphoric acid (II). This was prepared by the same way as I. In this case, no explosion occurred. Bp_2 67-68°. Yield : 61%.

Dimethyl hydrogen phosphite (III). III was prepared according to the description of Milobendzki *et al*[6]. Bp_7 51-53°. Yield : 34.5%.

Diethyl hydrogen phosphite (IV). Prepared similarly with III. Bp_{15} 78°. Yield : 62.5%.

Dimethyl β-cyanoethyl dithiophosphate (V). Pulverized sodium hydroxide (0.1 g) was added to the mixture of I (15.8 g, 0.1 mole), acrylonitrile (VI, 5.3 g, 0.1 mole) and hydroquinone (0.1 g) as an antioxydant. An exothermic reaction took place vigorously to yield a small amount of solid matter. After the initial reaction ceased, the mixture was stirred on a boiling water bath for further two hours. After cooling to room temperature, the reaction mixture was dissolved in ether, and the ethereal solution was washed with dilute sodium carbonate and water respectively, then dried over anhydrous sodium sulfate. After removal of ether, residual yellow oil (14.4g) was distilled *in vacuo* to give main fraction having boiling point 125-132° at 0.7 mm (8.8 g, 41.6%), besides a small amount of forerun (bp 0.7 58-62°). Redistilled sample was analyzed. $Bp_{0.5}$ 127-129°, n_D^{30} : 1.5350, d_4^{20} : 1.2647. Anal. Calcd. for $C_5H_{10}NO_2PS_2$: C, 28.22; H, 4.77; N, 6.64. Found : C, 28.22; H, 4.52; N, 6.29.

Diethyl β-cyanoethyl dithiophosphate (VII). VII was prepared by the same procedure as V,



starting from II (56 g, 0.3 mole) and VI (16.0 g). In this case, the reaction was carried out for six hours. On vacuum distillation of 62.0 g of yellow oil obtained from the reaction mixture, main fraction boiling at 145-146° (at 0.8 mm) was collected after removal of forerun (3.1 g, bp $_{0.2}$ 30-35°). Yield: 37.7 g (47.4%). Redistilled sample having boiling point 135-139° at 0.4-0.5 mm was analyzed. n_D^{20}: 1.503, d_4^{20}: 1.1757 (bp $_{3.5}$ 137-142°, n_D^{20}: 1.5195, d_4^{20}: 1.1704, in lit[1]). Anal. Calcd. for $C_7H_{14}NO_2PS_2$: C, 35.13; H, 5.89; N, 5.85. Found: C, 35.12; H, 5.64; N, 6.04.

Diethyl S-cyclopentenyl dithiophosphate (VIII). II (9.3 g) was added dropwise to the mixture of cyclopentadiene (3.5 g, 0.05 mole), 40% triethyl amine (0.2 cc) and hydroquinone (0.1 g). During exothermic reaction, the mixture was frequently shaked, and then warmed on a water bath at 60-70° for further ten hours. After cooling to room temperature, the reaction mixture was treated similarly as V. Distillation of crude material (9.4 g) gave 4.8 g of VIII boiling at 104-105° (at 0.03-0.04 mm), colorless oil. Anal. Calcd. for $C_9H_{17}O_2PS_2$: C, 42.83; H, 6.79. Found: C, 42.87; H, 6.63.

Diethyl S-dicylopentenyl dithiophosphate (IX). Starting from II (9.3 g, 0.05 mole), dicylopentadiene (X, 6.6 g), hydroquinone (0.1 g) and 40% trimethyl amine (0.3 cc), 13.5 g of crude material was obtained by the same way as VIII. A part of this oil (2.5 g) was distilled *in vacuo* to yield IX having bp $_{0.01}$ 136-137° (1.2 g, colorless oil). Anal. Calcd. for $C_{14}H_{23}O_2PS_2$: C, 52.79; H, 7.28. Found: C, 53.51; H, 7.31.

Dimethyl β-cyanoethyl phosphonate (XI). Saturated sodium methylate in methanol (30 drops) was added to the mixture of III (11 g, 0.1 mole) and VI (5.3 g), temperature of the mixture rising to 50°. The reaction mixture was heated on a water bath at 95° for two hours. On distillation *in vacuo*, 7.9 g of viscous oil was obtained after removal of unreacted VI (3.5 g). Three grams of the residual oil was distilled in vacuo in micro distilling flask to yield colorless oil (0.9 g) boiling at 106-110° (mainly 109-110°, at 0.2 mm). Total yield was 14.7% based on III. Anal. Calcd. for $C_5H_{10}NO_3P$: C, 36.80; H, 6.18; N, 8.58. Found: C, 36.16; H, 6.04; N, 9.06.

Diethyl β-cyanoethyl phosphonate (XII). Starting from IV (13.8 g, 0.1 mole), VI (5.3 g) and saturated sodium ethylate in ethanol (30 drops), XII was prepared by the same way as XI. Viscous oil (7.6 g) was obtained after the removal of unreacted IV (7.7 g). On distillation of 1.5 g of the residual oil *in vacuo*, colorless oil of XII (0.9 g) boiling at 95-99° (at 0.1 mm) was collected. Yield was 23.9% in total based on VI. Anal. Calcd. for $C_7H_{14}NO_3P$: C, 43.97; H, 7.32. N, 7.32; Found: C, 43.27; H, 7.20; N, 7.60.

Attempted synthesis of diethyl dicyclopentenyl phosphonate (XIII). X (6.6 g) was added to the mixture of IV (6.9 g) and 40% trimethyl amine (0.3 cc). Exothermic reaction did not take place. The mixture was heated at 65° for 20 hours. On distillation *in vacuo*, only a samll amount of unidentified substance (bp $_8$ 55°) was obtained after the recovery of unreacted IV (6.1 g). However XIII was not obtained.

Summary

In this study it was attempted to prepare some addition compounds of dialkyl dithiophosphoric acids or dialkyl hydrogen phosphites to olefinic compounds in order to evaluate their insecticidal effectiveness.

Acrylonitrile, cyclopentadiene and dicyclopentadiene reacted to dialkyl dithiophosphoric acids to yield the corresponding dithiophosphates in ca. 40% yield.

Similar reactions were studied with dialkyl hydrogen phosphites, and the corresponding dialkyl phosphonates were obtained from acrylonitrile in lower yield than in the case of dithiophosphates. It failed to prepare phosphonate from dicyclopentadiene.

Acknowledgement

We wish to express our thanks to Ph. Dr. Kizo Hiratsuka, Head of this Institute, for his kind encouragement and guidance thoroughout this work. Our thanks are also due to Mr. Ken'ichi Kojima for bioassay and helpful discussions concerning this work.

Literature

1) N. N. Mel'nikov, K. D. Shvestove-Shilov-

skaya: Zhur. Obshchei Khim. **23**, 1352 (1953); C. A. **48**, 9902 d (1954).
2) K. A. Gar, N. N. Mel'nikov, Yu. N. Fadeev, K. D. Shvestova-Shilovskaya: Doklady Akad. Nauk. S.S.S.R. **94**, 241 (1954): C.A. **48**, 6639 d (1654).
3) J.T. Cassaday: U. S. Pat. 2, 578, 652(1951): C. A **46**, 6139 c (1952).
4) G. Johnson, J. Fletcher, K. Nolan, J. Cassaday: J. Cassaday: J. Econ. Entomol. **45**, 279 (1952).
5) J. H. Fletcher *et al.*: J. Am. Chem. Soc. **72**, 2461 (1950).
6) Milobendzki, Sachnowski: Chem. Polsk. **15**, 34 (1917): of. G. M. Kosolapoff: "Organophosphorus Compounds", John Willey & Sons Inc., New York, 180 and 202 (1950).

Adsorptionability of Mineral Carriers in the Malathion and Methyl Parathion Dust Formulations. Studies on Organophosphorus Insecticides VII Seizo, MOTSUMOTO. (Fuji Chemical Industrial Co., LTD) Received Oct. 20, 1958 *Botyu-Kagaku* **23**, 211, 1958. (with English résumé, 218)

38. 増量剤の吸着性について

有機燐製剤に関する研究（第7報*） 松本清蔵（富士化学工業株式会社） 33. 10. 20 受理

農薬粉剤製造にあたり普通に使用されている増量剤を選択し，それらの吸着性を比較すべく芳香族吸着指数，アルコール比吸着指数，選択吸着性を測定した．又 benzeneazodiphenylamine の吸着，界面活性物質の吸着試験を実施した．その結果，増量剤の吸着性だけではマラソンの分解に対して有力なる原因にはならないが，表面酸性等の支配的因子が存在する場合は，これらが連合して更に強力な原因を構成することになることを推論すると共に二三の知見を得た．

著者は既報[1,2,3,4]において，主としてメチルパラチオン，マラソン粉剤の経時変化並びに有効成分分解防止について報告してきた．即ち此等の有効成分が貯蔵中において分解するのは珪酸アルミニウム誘導体を主体とする増量剤，カオリン，クレー，酸性白土等の場合には，それ等の表面酸性が分解の支配的因子であり同時に水分含有量も問題であり此の外に副因子として格子不整により生ずる lattice-bound-metal ion 即ち Fe^{+++}, Mg^{++}, Na^{+}, K^{+} 等の不純分の影響や貯蔵条件等が考えられ，又珪酸マグネシウム誘導体であるタルクの場合には，その触媒部分である $(H_2MgSiO_4)_x$ の anion part の強アルカリである Mg の影響が大きく表れることを指摘した．以上の外に，経験的に見て増量剤の表面積，表面特性と吸着性等を閑却してはいけない様に思われる．かくの如くその分解原因は複雑でありその分解過程には此等の諸因子が錯綜して関連的に作用しているのであろうと考える．そこで此等粉剤の分解防止の方法としては粉剤中の大部分を占める増量剤のメチルパラチオン等に対して適合性のあるものを探究選択することが第一手段であり，更に第三物質である安定剤を添加処理することである．従って増量剤の基礎的性質を把握することは極めて大切である．増量剤の表面特性，粒子の大小，粒子の形状，吸着能等が殺虫効力に或る影響を及ぼすことについては長沢，荒川[5]，等の研究の外 Wiggeleswoth, V. B[6~8] の報文等がある．増量剤の諸性質は実際に於いては千差万別であり，これらの性質が有効成分分解にも何らかの影響を及ぼすものと考えられる．著者の今迄の経験によれば吸着性の強いものの方がマラソン等の分解率が大きい様に思われるし殊に原体が液体であるか，又は少量の有機溶剤を用いて原体を溶解し impregnating proass により粉剤化する場合には，使用する増量剤の吸着性について充分検討しておく必要があると考える．

さて，溶液中における固体の吸着については Pratt[9]，水谷[10,11] 等は石油の脱色に用いる吸着剤の性能比較に際して芳香族吸着指数，アルコール吸着指数を提案している．又佐藤[12] はベントナイトに対する色素の吸着を研究しその表面の多重性を論じ，H. Weil-Malherbe と J. Weiss[13] はクレー，カオリン，ベントナイト等の原土及酸処理品につき吸着性を研究している．Eagle, Scott[14] 等は石油からの芳香族成分の分離を扱い，その選択吸着性を報告している．著者は農薬用各種増量剤につき前記文献を参考とし芳香族吸着指数，アルコール比吸着指数，選択吸着能を検討し表面酸性測定に使用している指示薬，Benzeneazodiphenyamine 及び安定剤の一つとして推賞している

* 松本・本田・大久保：応動昆 2 (3): 179～183 (1957).