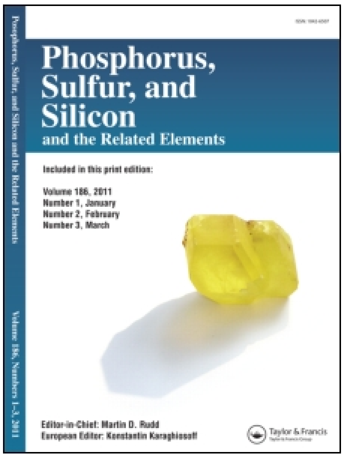


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOTOCHEMISTRY OF PESTICIDES, 13.[1] SOME PHOTOREACTIONS OF *O,O*-DIETHYL-*O*-(4-METHYL-2-OXO-2H-1-BENZOPYRAN-7-YL)-PHOSPHOROTHIOATE (POTASAN®)

Wafaa M. Abdou[a]; M. Refat Mahran[a]; Mahmoud M. Sidky[a]; Heinrich Wamhoff[b]
[a] National Research Centre, Laboratory of Pesticide Chemistry, Dokki, Cairo, A.R. Egypt [b] Institut für Organische Chemie und Biochemie der Universität Bonn, Bonn, Bundesrepublik, Deutschland

To cite this Article Abdou, Wafaa M. , Mahran, M. Refat , Sidky, Mahmoud M. and Wamhoff, Heinrich(1988) 'PHOTOCHEMISTRY OF PESTICIDES, 13.[1] SOME PHOTOREACTIONS OF *O,O*-DIETHYL-*O*-(4-METHYL-2-OXO-2H-1-BENZOPYRAN-7-YL)-PHOSPHOROTHIOATE (POTASAN®)', Phosphorus, Sulfur, and Silicon and the Related Elements, 39: 3, 199 — 203

To link to this Article: DOI: 10.1080/03086648808072875

URL: http://dx.doi.org/10.1080/03086648808072875

Phosphorus and Sulfur, 1988, Vol. 39, pp. 199–203
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOCHEMISTRY OF PESTICIDES, 13.[1] SOME PHOTOREACTIONS OF *O,O*-DIETHYL-*O*-(4-METHYL-2-OXO-2H-1-BENZOPYRAN-7-YL)-PHOSPHOROTHIOATE (POTASAN®)

WAFAA M. ABDOU, M. REFAT MAHRAN and
MAHMOUD M. SIDKY
National Research Centre, Laboratory of Pesticide Chemistry, El-Tahrir Street, Dokki, Cairo, A.R. Egypt

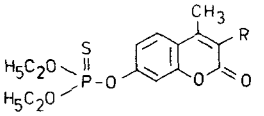
HEINRICH WAMHOFF*
Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, Bundesrepublik Deutschland

(Received April 18 1988)

UV-irradiation ($\lambda > 313$ nm) of *O,O*-diethyl-*O*-(4-methyl-2-oxo-2H-1-benzopyran-7-yl)-phosphorothioate (Potasan®) **1a** in chloroform and/or methanol with and without singlet oxygen results in the formation of the 2-oxo-2H-1-benzopyran-phosphate **2** the 3,3′-bipotasan dehydrodimer **3**, and 7-ethoxy-4-methyl-2-oxo-2H-1-benzopyran **4**; the mechanisms of formation, especially for **4** are discussed.

INTRODUCTION

Recently, we have described the photoconversion of the pesticide *O,O*-diethyl-*O*-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl)-phosphorothioate, Coumaphos **1b**.[2,3] It has been show that Coumaphos (**1b**) undergoes, most obviously from its triplet state, a regioselective photodimerization rather different from coumarin itself, to afford three dimers; a head-to-tail *anti* dimer, a corresponding phosphate, and a head-to-tail *syn* dimer.[2,3] Due to the increased interest in the environmental photochemistry and photodegradation of heterocyclic herbicides, pesticides, and insecticides, and as a part of our program on the photochemical studies of pesticides derived from organophosphorus compounds,[2–4] we have now choosen another related pesticide, *O,O*-diethyl-*O*-(4-methyl-2-oxo-2H-1-benzopyran-7-yl)-phosphorothioate, Potasan® **1a**, as an object for studying its photochemical behaviour.



1a: R=H (Potasan®)
1b: R=Cl (Coumaphos)

---

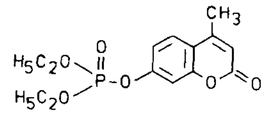
* Author to whom all correspondence should be addressed.

Potasan®, also marketed under the trade name Bayer E 838[5] is widely used as an insecticide,[5–7] an antihelminticum,[8] an ovicide,[9] a fungicide,[10] and a rodenticide.[11] With this present investigation, we wish to gain further information on the influence of substituents on the photochemical behaviour of coumarins.

RESULTS AND DISCUSSION

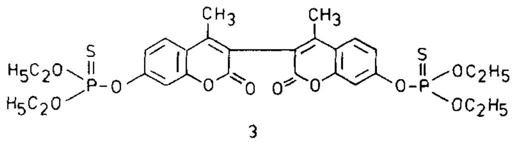
In a typical procedure,[2,3] a 1% chloroform and/or methanol solution of **1a** was irradiated in a Pyrex reactor ($\lambda > 313$ nm) with a Hg-high pressure lamp. The progress of the photoreaction was monitored by TLC. After 200 h (and 90% photoconversion of **1a**), column chromatography gave three photoproducts **2–4**, in sequence.

The first product, a yellow liquid (**2**, *ca.* 12% yield) was easily identified as Potasan® phosphate **2** by comparison with an authentic sample.[6,12] This type of thiophosphate → phosphate oxidation is commonly recognized during insolation[5] or photoreactions.[3–6]



2

The second product isolated, **3** (a yellow crystalline compound, mp 120°C *ca.* 8% yield) was shown by elemental analysis and high resolution MS to possess the elemental composition $C_{28}H_{32}O_{10}P_2S_2$ (654.6; m/z 654, M^+). The ^1H NMR spectrum of **3** is simple indicating the symmetrical nature of the molecule and pointing to a 3,3′-linkage. Thus, the aromatic multiplet centered at $\delta 7.0$–7.6 ppm, was integrated to six protons; the quadruplet at $\delta 6.23$ ppm ($J_{HH} = 1.5$ Hz) assigned[13] to 3-H in Potasan (**1a**) is absent in photoproduct **3**. Accordingly, the singlet at $\delta 2.58$ ppm (s, 6H) is attributed to both methyl groups attached to sp_2-hybridized C-atoms.[13] This observation, that both methyl groups appear as one singlet, presents unambiguous evidence for the absence of the methine protons 3-H and 3′-H (for comparison: **1a**: $\delta 2.33$ ppm (d, 3-H, $J_{HH} = 1.5$ Hz). Accordingly, the thiophosphate ethoxy-CH_2 (8H) appear as doublets of quadruplets ($\delta 4.26$ ppm) while the ethoxy-CH_3 (12H) display a doublet of triplets ($\delta 1.37$ ppm; $J_{PH} = 11.5$, $J_{HH} = 0.8$ Hz); the ^{31}P NMR signal at $\delta + 62.53$ ppm is in complete agreement with usual thiophosphate shifts.[14] From these data, it follows **3** constitutes an *O,O,O,O*-Tetraethyl-*O,O*-4,4′-dimethyl-2,2′-dioxo-(3,3′-bi-2H-1-benzopyran-7,7′-diyl)-diphosphorothioate. A few 3,3′-bi(2H-1-benzopyran)-2,2′-diones have been sparingly described in the literature as fluorescent whiteners[15] and as compounds of pharmaceutical interest;[16] to our knowledge **3** is the first 3,3′-bi-coumarine obtained in the course of a photolysis reaction instead of an expected typical cyclobutane dimer.[2,3,17–20]



3

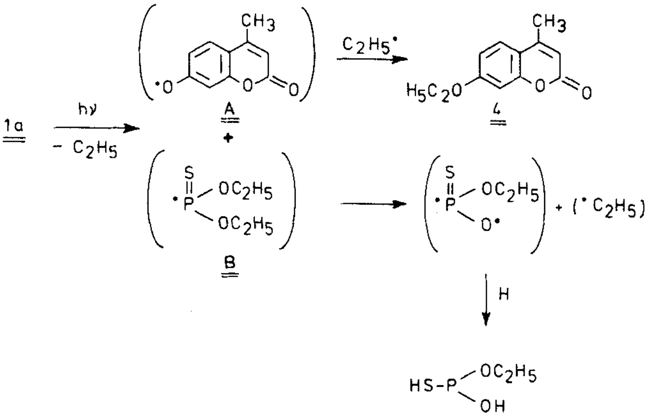
The last product obtained, **4**, turned out to be the major product (*ca.* 23% yield) forming colorless crystals of mp 115°C, and was established to be 7-ethoxy-4-methylcoumarin by the following physical and spectral data:

(1) Elemental analysis and MS support the molecular formula $C_{12}H_{12}O_3$ (204.2); accordingly MS: $m/z = 204$ (M^+);

(2) The IR-spectrum of **4** reveals absorptions at 1740 (C=O, lactone) and 1625 cm^{-1} ($C{=}C_{arom.}$);

(3) The ^1H NMR spectrum reveals (phosphorus uncoupled) triplets and quadruplets at $\delta 1.46$ (3H, ethoxy-CH_3) and 4.11 ppm (2H, ethoxy-CH_2); the 4-methyl group and 3-H showed the typical allylic coupling pattern ($\delta 2.64$ (3H, d, $J_{HH} = 1.5$ Hz); 6.28 (1H, q, $J_{HH} = 1.5$ Hz).[13]

Obviously, **1a** upon UV-irradiation undergoes a homolytic cleavage of the 7-O-P bond generating intermediary radical species, such as **A** and **B**. This transient **A** then produces **4** by intermolecular recombination with an ethyl radical, formed by further photolysis of **B**.



SCHEME 1

Related photochemical dealkylation processes of phosphites, phosphates, and thiophosphates are known in the literature.[5,6]

In the presence of singlet oxygen (O_2 circulated into the reaction mixture using methylene blue as sensitizer), the yields of the photoproducts **2–4** are significantly increased, and only 5% of Potasan® **1a** could be recovered unreacted (cf. Experimental Part).

CONCLUSION

As a consequence following from the photoreactions reported above, two main pathways of photodegradation and oxidation might be discussed: the first is the photoinduced dehydrodimerization of the coumarin moieties, forming the (3,3′-bi-2H-1-benzopyrane)-2,2′-dione (bi-3,3′-Potasan®) **3**.

Another degradation pathway is the photooxidation of the thiophosphate rest leading to the oxygen analog **2** of Potasan®. In the case that both forementioned pathways of phototransformation occur sluggishly, the side chain homolysis can compete effectively, furnishing the break down product **4**.

Although, singlet oxygen seems not to be involved in these photolysis pathways, it shows a remarkably decreasing effect on the reaction time, while the yield of the photoproducts is increased.

Furthermore, the results of the present investigation reveal that the products formed during this photolysis of Potasan® **1a** are clearly different from those reported for the photodegradation of Coumaphos **1b**: **1b** undergoes classical but regioselective (T_1-intermediate) $[2+2 \rightarrow 4]$-dimerization, while Potasan® **1a** lacking the 3-chloro atom, affords upon UV-irradiation a dehydrodimerized bi-3,3′-Potasan® **3**, which has not yet been found upon UV-irradiation of a coumarin moiety.

EXPERIMENTAL

General Data. All melting points are uncorrected. Potasan® **1a** was supplied by the Bayer AG, D-5090 Leverkusen. – IR(KBr): Perkin–Elmer 157 G. – ^{1}H NMR ($CDCl_3$): Bruker WH-90 (δ-values, TMS as internal standard). – ^{31}P NMR ($CDCl_3$, vs 85% H_3PO_4): Varian CFT-20. – MS(70 eV): MS-50 of Kratos (A.E.I.). – Microanalysis: Mikroanalytisches Laboratorium Pascher, Remagen. – TLC eluent system: toluene–ethyl acetate–ethanol (6:3:1, v/v/v).

Photolysis of Potasan® **1a**. A solution of Potasan® **1a** (3g, 9 mmol) in chloroform or methanol—best results in methanol—was irradiated with a Hg-high pressure lamp in a Pyrex reactor, while the progress of the reaction course was monitored by TLC. After 200 h (ca. 90% photoconversion of **1a**), the reaction mixture was evaporated *in vacuo*. The residue obtained (yellow oil) was chromatographed on silica gel; eluent system: toluene, then toluene containing increasing amounts of ethyl acetate.

Fraction (100% toluene), provided 370 mg (11.8%) of a pale yellow liquid, elucidated as the oxygen analog **2** of Potasan® (comparative TLC, IR, and ^{1}H NMR spectra with an authentic sample[6,12]). MS: m/z 312 (M^+).

Fraction (95:5, v/v) gave 315 mg (10.56%) of unchanged **1a**, mp 38°C (lit mp 38°C[6,21]); MS: m/z 328 (M^+).

Fraction (90:10, v/v) afforded a yellow crystalline material 252 mg (8.4%), which was recrystallized from acetone to give pale-yellow crystals of mp 120°C and identified as 3,3′-dehydrodimer **3**. – IR 1765 1025 cm^{-1}; ^{1}H NMR δ1.37 (dt, $POCH_2CH_3$, $J_{PH} = 11.5$, $J_{HH} = 0.8$ Hz), 2.58 (s, 4-CH_3), 4.26 (dq, $POCH_2CH_3$, $J_{PH} = 11.5$, $J_{HH} = 0.8$ Hz), 7.0–7.6 (m, $H_{ar.}$); ^{31}P NMR δ62.35 ppm; MS m/z 654 (M^+); Anal. Calcd. for $C_{28}H_{32}O_{10}P_2S_2$ (654.4): C, 51.36; H, 4.92; P, 9.46; S, 9.85. Found: C, 51.08; H, 4.78; P, 9.33; S, 9.47.

Fraction (70:30, v/v), contained a colorless crystalline product, 429 mg (23.2%), recrystallized from ethanol; mp 115°C, proved to be 7-ethoxy-4-methyl-2-oxo-2H-1-benzopyran (7-ethoxy-4-methyl coumarin) **4**. – IR 1740, 1625; ^{1}H NMR δ1.46 (t, ethoxy-CH_3), 2.64 (d, 4-CH_3, $J_{HH} = 1.5$ Hz), 4.11 (q, ethoxy-CH_2), 6.28 (*q*, 3-*H*, $J_{HH} = 1.5$ Hz), 7.1–7.5 (m, $H_{ar.}$). – MS: m/z 204 (M^+); Anal. Calcd. for $C_{12}H_{12}O_3$ (204.2): C, 70.57; H, 5.92. Found: C, 70.23; H, 5.89.

Photolysis of Potasan® **1a** *in the Presence of Singlet Oxygen.* A solution of Potasan® **1a** (3g, 9 mmol) in methanol (300 ml) was irradiated for 150 h while oxygen was steadily circulated in the solution containing 30 mg of methylene blue. Working up the photolysate as described above, resulted in isolation and identification of **2** (376 mg, 13.2%), unchanged **1a** (170 mg, 5.7%), 3,3′-dehydrodimer **3** (294 mg, 9.8%), and **4** (510 mg, 27.5%), respectively.

ACKNOWLEDGMENT

This work was supported by the ASRT, Cairo, the Fonds der Chemischen Industrie and the Bayer AG. W.M.A. thanks the Heinrich–Hertz–Stiftung for granting a reserarch fellowship. We are grateful to Prof. Dr. H. Hulpke, Leverkusen, for helpful discussions.

REFERENCES AND NOTES

1. Part 12 of this Series: W. M. Abdou, M. M. Sidky and H. Wamhoff, *Z. Naturforsch.* **42b,** 1153 (1987).
2. W. M. Abdou, L. Born, H. Hulpke, M. R. Mahran, M. M. Sidky and H. Wamhoff, *Phosphorus and Sulfur,* **29,** 179 (1987).
3. W. M. Abdou, M. M. Sidky and H. Wamhoff, *J. Agric. Food Chem.*, **36,** (1988), in press.
4. W. M. Abdou, M. M. Sidky and H. Wamhoff, *Z. Naturforsch.*, **42b,** 907 (1987); H. Wamhoff, W. M. Abdou and M. Zahran, *J. Agric. Food Chem.*, **36,** 205 (1988).
5. K. H. Büchel (ed.), *Chemistry of Pesticides* (Wiley-Interscience, New York, 1983), p. 82.
6. G. Schrader (ed.), *Die Entwicklung neuer insektizider Phosphorsäureester* (Verlag Chemie, Weinheim, 1963); N. N. Melnikov, *Chemistry of Pesticides,* F. A. Gunther and J. D. Gunther (eds.) (Springer, New York, 1971).
7. G. Schrader, *Angew. Chem.*, **62,** 471 (1950); *Monograph No.* 62, 62pp.; J. R. Busvine, *Entomol. Exptl. et Appl.*, **2,** 58 (1959); *Chem. Abstr.*, **53,** 459b (1958).
8. C. O. Knowles and J. E. Casida, *J. Agr. Food Chem.*, **14,** 566 (1966).
9. A. H. M. Kirby and M. Bennett, *Ann. Rept. East Malling Research Sta., Kent,* 1950, 164; *Chem. Abstr.*, **47,** 7150g (1953).
10. A. H. M. Kirby and M. Bennett, *ibid.* 1951, 183; *Chem. Abstr.*, **48,** 5425 f (1954).
11. J. P. Frawley, E. C. Hagan and O. G. Fitzhugh, *J. Pharmacol. Exptl. Therap.*, **105,** 156 (1952); *Chem. Abstr.*, **46,** 9200 b (1952).
12. Cf. G. Losco and C. A. Ferri, *Gazz. Chim. Ital.*, **89,** 1298 (1959).
13. M. R. Mahran and M. M. Sidky, *Org. Magn. Reson.*, **15,** 208 (1981).
14. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, ^{31}*P Nuclear Magnetic Resonance* (Wiley-Interscience, New York, 1967).
15. L. L. Woods and S. M. Shamma, *J. Chem. Eng. Data,* **15,** 355 (1970); A. Chandrasenkhar, S. Padmanabhan, S. Seshadri, *Dyes Pigm.*, **7,** 13 (1986); *Chem. Abstr.*, **104,** 188 143 s (1986).
16. F. Eiden and L. Prielipp, *Arch. Pharm (Weinheim),* **310,** 109 (1977); *Ger. Offenl. DE* 241 4604 (1975); *Chem. Abstr.*, **84,** 30 893 v (1975).
17. R. Anet. *Canad. J. Chem.*, **40,** 1249 (1962).
18. G. S. Hammond, C. A. Stout and A. A. Lamola, *J. Am. Chem. Soc.*, **86,** 3103 (1964).
19. H. Morrison, H. Curtis and T. McDowell, *J. Am. Chem. Soc.*, **88,** 5415 (1966).
20. R. Hoffman, P. Wells and H. Morrison, *J. Org. Chem.*, **36,** 1 (1971).
21. S. H. Yang, T. C. Chen, C. M. Li, H. L. Wang, J. C. Huang, C. C. Tang, T. L. Liu and C. P. Chang, *Hua Hsueh Hsueh Pao,* **31,** 399 (1965); *Chem. Abstr.*, **64,** 11 240h (1966).