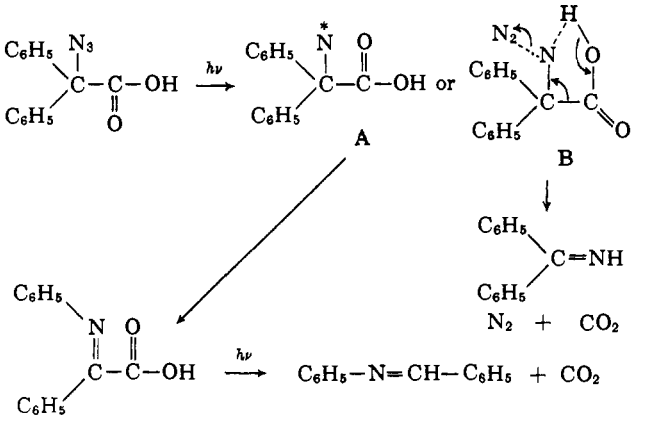
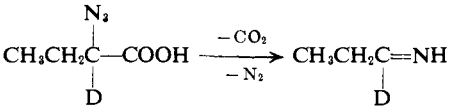
(as the 2,4-DNP), but no acetaldehyde 2,4-DNP could be detected. Photolysis of azidodiphenylacetic acid yielded carbon dioxide in 60% yield. Treatment of the photolysate with 2,4-dinitrophenylhydrazine in acid solution yielded a mixture of benzophenone 2,4-DNP (20%) and benzaldehyde 2,4-DNP (30%). Yields are based on the starting azido acid. Thus, in this system phenyl group migration competes effectively with loss of carbon dioxide. The origin of the benzaldehyde was established by the fact that separate irradiation of benzoylformic acid phenylimine leads to 80% decarboxylation.[6] Hydrolytic work-up of the photolysate yielded benzaldehyde (45% as the 2,4-DNP) and aniline (60% as benzanilide). Benzaldehyde phenylimine was detected spectroscopically as a product of this photolysis. The photodecarboxylation of azidodiphenylacetic acid probably proceeds *via* a dual mechanism involving both direct loss of carbon dioxide and also phenyl group migration followed by decarboxylation.



A concerted loss of nitrogen and carbon dioxide is possible although not required by the present results. The operational difference between A and B is that A is an intermediate and B is a transition state. If nitrogen and carbon dioxide are lost in the same transition state then a discrete alkyl nitrene such as A need not occur.[7]

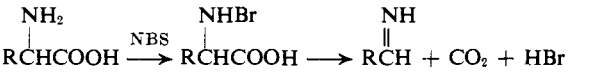
Related photolyses of the ethyl esters of the α-azido acids were also carried out. No decarboxylation was observed with the esters; the principal products were α-imino esters and small yields of α-amino esters. Thus ethyl α-azidobutyrate yielded ethyl α-ketobutyrate (25% as the 2,4-DNP from the imine) and ethyl α-azidovalerate yielded ethyl α-ketovalerate imine (25%) along with ethyl (±)-α-aminovalerate (5%). No ethyl (±)-proline was observed.[5,8]

The question of whether the photodecarboxylation of α-azido acids bearing an α-hydrogen proceeds *via* direct loss of carbon dioxide or, alternatively, by photolysis of an intermediary α-imino acid is complicated by the fact that either pathway leads to the same products. The latter route is plausible both on the basis of the observed photodecarboxylation of N-aryl-α-imino acids and also due to the known photochemical decarboxylation reaction of α-keto acid.[10] In order to learn to what extent photodecarboxylation of α-azido acids bearing an α-hydrogen proceeds by direct loss of carbon dioxide, the photolysis of α-deuterio-α-azidobutyric acid[11] was studied. The propionaldehyde 2,4-DNP obtained in this photolysis was found to contain 58% deuterium.[12] Nuclear magnetic resonance analysis indicated that the deuterium was at the aldehydic carbon atom. Intermediacy of an α-imino acid requires loss of deuterium in the 1,2-shift from carbon to nitrogen.



The observed result indicates that the direct mechanism is operative at least to the extent of 50%. It is possible that the undeuterated propionaldehyde may result from photodecarboxylation of the α-imino acid; this point is currently under investigation.

Finally, it may be noted that the photodecarboxylation of α-azido acids resembles the bromodecarboxylation reaction observed upon treatment of α-amino acids with N-bromosuccinimide.[13]



(6) The photochemically induced decarboxylation of N-alkyl- and N-aryl-α-imino acids will be discussed in a separate publication. Irradiation of benzaldehyde phenylimine in 98% sulfuric acid yields phenanthridine (G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Letters*, **No. 49**, 3711 (1964)).

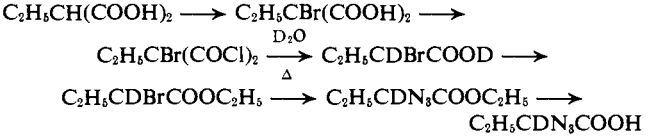
(7) In methanol solution, the α-azido acids would be expected to be partially dissociated. The question arises whether the conjugate base or undissociated acid is the species which undergoes decarboxylation. However, since photodecarboxylation occurs in benzene solution it is clear that the carboxylate anion is not required. Also, one must recognize the possibility of photosensitization occurring with benzene as solvent. We thank the referees for calling both points to our attention.

(8) Barton and Morgan[5] have found that photolysis of ethyl (±)-α-azidopropionate yielded ethyl pyruvate imine (34%). Kuhn[9] studied the irradiation of racemic N,N-dimethyl-α-azidopropionamide with dextro and levo circularly polarized light as a model experiment for the formation of optically active compounds *de novo*.

(9) W. Kuhn and E. Knopf, *Z. physik. Chem.*, **7B**, 292 (1930); *Naturwiss.*, **18**, 183 (1930).

(10) P. A. Leermakers and P. A. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).

(11) α-Deuterio-α-azidobutyric acid was synthesized



(12) Deuterium analysis was performed by J. Nemeth, Urbana, Ill.

(13) N. Konigsberg, G. Stevenson, and J. M. Luck, *J. Biol. Chem.*, **235**, 1341 (1960).

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Evidence for the Conversion of *o,p*-DDT (1,1,1-Trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane) to *p,p'*-DDT (1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane in Rats

Sir:

In a recent report[1] it was shown that reductive dechlorination of DDT to DDD (1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethane) occurs in the liver of the rat consuming a diet to which DDT had been added. In these experiments both *ortho,para* and *para,para'* isomers of DDT were fed. It was noted that irrespective of the isomer fed only *p,p'*-DDD was found in

(1) A. K. Klein, E. P. Laug, P. R. Datta, J. O. Watts, and J. T. Chen, *J. Assoc. Offic. Agr. Chemists*, **47**, 1129 (1964).

Table I. *o,p*- and *p,p'*-DDT in the Abdominal Fat of Rats Fed *o,p*-DDT[a]

Rat	DDT in fat, p.p.m. *o,p*	*p,p'*
	Experimental	
F	3.6	36.5
F	8.9	75.0
M	1.4	29.5
M	7.4	4.4
M	1.1	20.1
M	4.6	32.0
	Av. 4.5	31.3
	Control[b]	
F	0.15	4.8
F	0.15	7.5
M	0.20	4.0
M	0.15	4.6
M	0.15	8.8
	Av. 0.16	5.9

[a] *o,p*-DDT, 50 p.p.m. for 12 weeks. [b] Diet contains 2.7×10^{-3} p.p.m. of *o,p*-DDT, 9.4×10^{-3} p.p.m. of *p,p'*-DDT.

Table II. *o,p*- and *p,p'*-DDT in the Abdominal Fat of Rats Fed *o,p*-DDT[a]

Rat	DDT in fat, p.p.m. *o,p*	*p,p'*
	Experimental	
F	8.3	11.8
F	4.0	2.5
F	7.3	11.8
M	3.3	8.4
M	3.3	12.1
M	3.5	14.8
M	3.4	12.7
	Av. 4.9	10.6
	Control[b]	
F	0.04	0.30
M	0.10	0.73
	Av. 0.07	0.52

[a] *o,p*-DDT, 25 p.p.m. for 9 weeks. [b] Diet contains 8×10^{-4} p.p.m. of *o,p*-DDT, 2.4×10^{-3} p.p.m. of *p,p'*-DDT.

the liver, and relatively small quantities of *o,p*-DDT compared to *p,p'*-DDT in the abdominal fat. While the isomeric transformation of *o,p*-DDT to *p,p'*-DDT by chemical reactions *in vitro* has not been reported in the literature, we wish to present evidence that strongly indicates that such a conversion may be biologically mediated.

Experiments were conducted on two groups of mature Sprague Dawley rats. In the first experiment, the animals were maintained for 12 weeks on a standard laboratory chow, spiked to contain 50 p.p.m. of *o,p*-DDT. In the second experiment run approximately a year later to check the earlier findings, the animals were kept for 9 weeks on a diet containing 25 p.p.m. of *o,p*-DDT. Control rats eating only the unspiked basic diet were run concurrently with each experiment. It is most important to emphasize that in the second experiment the basic diet was modified in such a way as to exclude nearly all of the DDT residuals, small quantities of which had been found to contaminate the standard laboratory chow used in the first experiment.

At the end of the respective exposure periods the animals were sacrificed, and abdominal fat was removed for analysis. All fat samples were extracted with ethyl ether, and the extract was defatted with

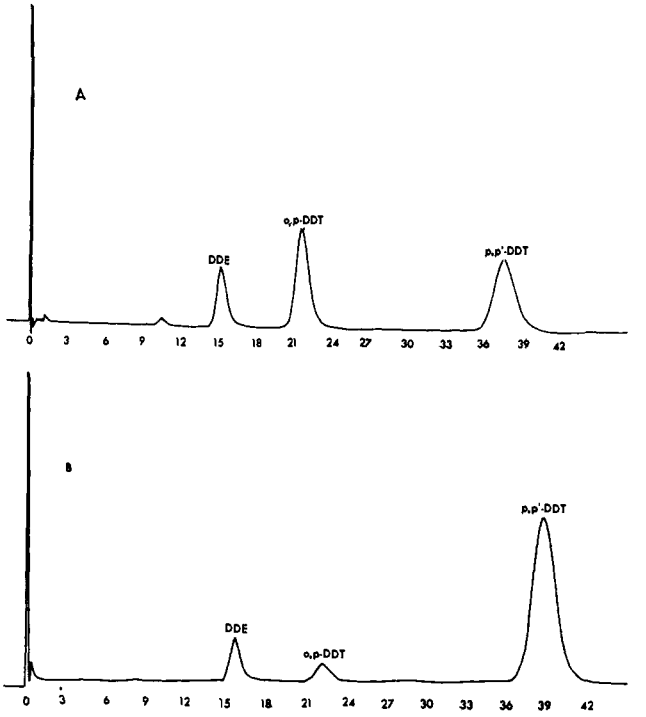

Figure 1. A, standard: 3 μl. injected of a solution containing 1.0 μg./ml. of *p,p'*-DDT (retention time 37.5 min.), 1.0 μg./ml. of *o,p*-DDT (21.5 min.), and 0.2 μg./ml. of DDE (1,1-dichloro-2,2-bis-(*p*-chlorophenyl)ethylene) (15 min.); B, experimental: 0.17 g./ml. of sample; 2 μl. injected.

acetonitrile and further purified by selective solvent elution from an activated Florisil column preparatory to analyses for DDT by gas chromatography.[2]

Because an alternate interpretation of these results hinges on the purity of the *ortho,para* isomer of DDT, this point was examined with special care. Two samples of reference grade *o,p*-DDT from two independent sources, each prepared by a different method, were examined by electron-capture gas chromatography for *para,para'* isomer contamination. No *p,p'*-DDT isomer could be detected in either when 1 μg. of *o,p*-DDT was analyzed. Furthermore, it was determined that a lower limit of as little as 0.0005 μg. of *p,p'*-DDT was detectable. If it is assumed that this level of *p,p'*-DDT was present in the reference grade of *o,p*-DDT fed, a 12-week accumulation of this contaminant in the fat of the experimental rats fed a 50-p.p.m. level of *o,p*-DDT could have contributed no more than 0.7 p.p.m.

Figure 1 gives a representative tracing of fat prepared from a rat that consumed *o,p*-DDT. A standard prepared from a mixture of equal quantities of *o,p*- and *p,p'*-DDT is included for comparison. It can be seen that even though only *o,p*-DDT was fed, a much larger proportion of DDT was recovered in the fat as *para,para'* than *ortho,para* isomer.

In Table I are presented the analyses of abdominal fat from rats that had consumed 50 p.p.m. of *o,p*-DDT in their diet for 12 weeks. On the average and with one exception, about seven times more *p,p'*-DDT than *o,p*-DDT was found. Since the background diet of these animals contained measurable amounts of *o,p*- and *p,p'*-DDT, it is expected that the control fat would

(2) A. K. Klein, J. O. Watts, and J. N. Damico, *J. Assoc., Offic., Agr. Chemists, ibid.*, **46**, 165 (1963).

also contain *p,p'*-DDT. However, these levels are too low to account for the disproportionate ratios.

In Table II are presented the results of an experiment where the exposure to *o,p*-DDT was repeated at a lower level and for a shorter time. While the excess *p,p'*- over the *o,p*-DDT is smaller under these conditions (approximately 2:1), the possible contribution from diet residuals has been reduced about tenfold. Here it is even more apparent that the explanation for the findings in both experiments cannot be attributed to the presence of contaminating sources of *p,p'*-DDT in the control diets.

In order to confirm that the *p,p'*-DDT found in fat by gas chromatography and presumed to originate from *o,p*-DDT is, in fact, *p,p'*-DDT, independent identification was made by micro infrared spectroscopy. The infrared spectrum of *p,p'*-DDT derived from fat was compared with a standard crystalline preparation of *p,p'*-DDT. Precise correspondence of the strong bands at 9.15, 9.85, 12.80, and 13.05 μ and the medium strength bands at 11.80 and 11.95 μ was observed. These bands are characteristic of the *para,para'* isomer of DDT. Comparison with a standard crystalline preparation of *o,p*-DDT showed that the bands at 9.51 and 9.62 μ characteristic for this isomer were absent.

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Organic Phosphorus–Sulfur Chemistry. I. A Novel Synthesis of Tertiary Trithiophosphites

Sir:

Trialkyl trithiophosphites have been prepared by the interaction of yellow phosphorus and dialkyl disulfides at 170–210°.[1] Since homolysis of disulfides occurs at these temperatures,[2] the reaction presumably involves free radicals.

We wish to report an ionic reaction of yellow phosphorus with organic disulfides in a dipolar aprotic

$$P_4 + 6RSSR \xrightarrow{B^-} 4(RS)_3P$$

solvent. Unlike the thermal process,[1] which requires extended reaction time and often superatmospheric pressures, the new reaction proceeds exceptionally smoothly under very mild conditions. A general procedure is as follows. About 1 ml. of 15 *N* potassium hydroxide is added to a stirred mixture of 1 g.-atom of finely divided phosphorus and 1.5 moles of disulfide in 500 ml. of acetone at room temperature under nitrogen. The reaction is slightly exothermic and is usually complete within 30 min. The product is isolated by vacuum distillation in greater than 90% yield. If yellow phosphorus is present in excess, dark solids having high phosphorus content are formed at the end of the reaction in addition to the trithiophosphite. The reaction may be carried out more conveniently by using molten phosphorus (m.p. 44°). The reaction is generally applicable to simple aliphatic and aromatic disulfides.

Group I-A bases such as hydroxides, alkoxides, mercaptides, alkyls, amides, hydrides, and phosphides are effective catalysts. Grignard reagents and calcium amide may also be used as catalysts. The reaction is rapid in dipolar aprotic solvents such as acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide; but it proceeds extremely slowly in protic solvents such as methanol or in ethereal solvents such as tetrahydrofuran.

Data indicate that the reaction most probably involves bimolecular nucleophilic substitutions at phosphorus and at sulfur. The detailed mechanism is necessarily complex, since all of the six P–P bonds in the P_4 tetrahedron must be progressively cleaved, with each cleavage producing at least one new organophosphorus intermediate.

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About the Ahrland–Chatt–Davies Classification of Rhodium and Iridium into Type (a) or (b) Central Atoms

Sir:

The Ahrland–Chatt–Davies[1] classification of the elements and ions according to their relative affinities for ligands, together with Pearson's[2] generalization that hard (type (a)) acids prefer to associate with hard bases, and soft (type (b)) acids prefer soft bases, has proved to be a useful tool for explaining or predicting the stability of compounds. For elements on the border line where it is not possible to assign hardness or softness unambiguously, several explanations can be found as to why an atom or ion sometimes exhibits hard and sometimes soft character. These include the ionization state,[3] the steric factor,[4] and the nature of other ligands in the complex.[3,5]

Ahrland, Chatt, and Davies[1] classify rhodium as a type (b) element, but close to the border line of type (a), and iridium as class (b). Pearson[2] does not classify rhodium, and derives for iridium(III) class (a) behavior on the basis of equilibrium data[6] for the hydrolysis of $[Ir(NH_3)_5X]^{2+}$, where X refers to a halide ion.

Thiocyanate when coordinated to these metals may serve as a test case for this classification since this anion is known to be a difunctional ligand which can be attached to the metal cation either through the soft sulfur or the hard nitrogen atom. This property together with Pearson's rule that hard acids prefer hard bases and soft acids prefer soft bases facilitates the description of these central atoms as relatively more hard or

(1) D. R. Stevens and R. S. Spindt, U. S. Patent 2,542,370 (1951); G. D. McLeod, U. S. Patent 2,768,194 (1956); G. D. McLeod and E. L. d'Ouville, U. S. Patent 2,819,290 (1958).
(2) For a summary of the evidence, see W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y. 1962, pp. 42–45.

(1) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).
(2) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(3) C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).
(4) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).
(5) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).
(6) A. B. Lamb and L. T. Fairhall, *J. Am. Chem. Soc.*, **45**, 378 (1923).