A solution of *cis,cis*-1,5-cyclooctadiene (90 g., 0.833 mole) and *t*-butyl peroxide (11.0 g., 0.075 mole) was added over a period of 24 hr. to a heated (137 ± 2°) stirred mixture of *t*-butylformamide[6] (3.03 kg., 30 moles), *cis,cis*-1,5-cyclooctadiene (18 g., 0.167 mole), and *t*-butyl peroxide (2.92 g., 0.02 mole). After removal of peroxide decomposition products (acetone, *t*-butyl alcohol), unchanged *cis,cis*-1,5-cyclooctadiene (~5 g.), and *t*-butylformamide by distillation, the dark-colored residue was treated with heptane to give crude (95–120 g., 46–57%)[7] N-*t*-butyl-*exo,cis*-bicyclo[3.3.0]octane-2-carboxamide (I) (m.p. 130–134°) which after recrystallization from pentane or sublimation melted at 134–135°[8]; λ_{max} 3.08, 3.30, 6.11, 6.48 μ. N.m.r. analysis[9] showed a single peak at 5.31 p.p.m. (NH proton), a broad peak centered at 2.53 p.p.m. (attributable in part to C-2 proton), several unassigned peaks between 1.51 and 1.8 p.p.m. (CH_2 protons), and a sharp single peak at 1.29 p.p.m. (CH_3 protons). N-*t*-Butylcyclooctanecarboxamide, m.p. 150–151° (prepared from cyclooctene and N-*t*-butylformamide), showed a singlet at 5.24 p.p.m. (NH proton), no peak at 2.53 p.p.m., a broad ill-defined peak from 1.53 (max.) to 1.8 p.p.m. (CH_2 protons), and a sharp singlet at 1.29 p.p.m. (CH_3 protons). The n.m.r. spectra are easily distinguishable.

All attempts[10] to saponify I were fruitless. Authentic I prepared from the authentic precursor acid[11] (*via* the acid chloride) and *t*-butylamine was indistinguishable from the free-radical product (n.m.r., infrared, melting point, mixture melting point).

Reaction of *cis,cis*-1,5-cyclooctadiene with methyl formate[12] and dimethylformamide[6] in the presence of *t*-butyl peroxide gave in low yield the expected methyl *exo,cis*-bicyclo[3.3.0]octane-2-carboxylate and a 1:1 mixture of N,N-dimethyl-*exo,cis*-bicyclo[3.3.0]octane-2-carboxamide and N-methyl-N-formyl-*exo,cis*-bicyclo[3.3.0]octane-2-methylamine, respectively.

Diethyl[5] (and dibutyl) phosphonate and *cis,cis*-1,5-cyclooctadiene in the presence of *t*-butyl peroxide gave diethyl *exo,cis*-bicyclo[3.3.0]octane-2-phosphonate (60%, b.p. 92–94° at 0.5 mm., $n^{25}D$ 1.4680) and the corresponding dibutyl ester (55%, b.p. 126° at 0.3 mm., $n^{25}D$ 1.4650). Extended hydrolysis in a hydrochloric–acetic acid mixture gave *exo,cis*-bicyclo[3.3.0]octane-2-phosphonic acid, m.p. 101.5–102.5°. N.m.r. analysis[9] on the ethyl ester showed a quartet centered at 1.3 p.p.m. (CH_3 protons in ethyl group), a broad peak centered at 2.48 p.p.m. (in part due to C-2 proton), and other unassigned peaks from 1.55 (max.) to 2.0 p.p.m. (CH_2 protons in ring, etc.). The butyl ester showed a quartet centered at 3.93 p.p.m. (CH_2 protons in butoxy group), a broad peak centered at 2.54 p.p.m. (C-2 proton), and other unassigned peaks from 1.55 (max.) to 2.0 p.p.m. The free acid showed a sharp peak at 11.6 p.p.m. (acid protons), a broad peak centered at 2.52 p.p.m. (C-2 proton), complete absence of vinyl protons, and unassigned peaks between 1.55 and 2.0 p.p.m. Cyclooctanephosphonic acid did not display a peak at 2.52 p.p.m. The phosphonic acid and esters are inert toward the usual oxidizing agents, bromine, and hydrogen over palladium.

The generality of free-radical cyclo-additions to *cis,cis*-1,5-cyclooctadiene was further established by reactions with acetaldehyde, thiophenol, and piperidine.

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(6) L. Friedman and H. Shechter, *Tetrahedron Letters*, 238 (1961).

(7) The residue consisted of higher telomers, presumably N-*t*-butylpoly(bicyclo[3.3.0]octane)-2-carboxamide (n.m.r. analysis).

(8) Satisfactory elemental analyses were obtained for all new compounds.

(9) The assistance of Dr. W. R. Ritchey, Research Laboratories, Standard Oil Co., Ohio is gratefully acknowledged.

(10) Fused potassium hydroxide at 200°; potassium hydroxide in triethanolamine at 250°; phosphoric acid at 100, 150°; polyphosphoric acid at 120°; at 200° total destruction of the amide occurred.

(11) A. C. Cope and M. Brown, *J. Am. Chem. Soc.*, **80**, 2859 (1958).

(12) W. H. Urry and E. S. Huyser, *ibid.*, **75**, 4876 (1953).

On the Formation of Pyrophosphate from Quinol Phosphates in Dimethylformamide Solution

Sir:

Quinol phosphates have been suggested[1] as the active agents for oxidative phosphorylation in biological systems. In the presence of an oxidizing agent, such as air or bromine, various naphthalenediol phosphates have been shown[2,3] to be capable of phosphorylating alcohols and other substrates. However, it was found,[4] using a solvent enriched in oxygen-18, that the breakdown of a model compound, 2,3-dimethylnaphthalenediol 1-phosphate (4-hydroxy-2,3-dimethyl 1-phosphate, I), undergoes "oxidative hydrolysis" in a complex fashion, only 30% of the phosphate being produced in the form of metaphosphate, the phosphorylating entity.

In order to study this reaction under simpler and more easily controlled conditions, it has now been run in an anhydrous solvent. On adding excess bromine to a solution of I in dry dimethylformamide (DMF) in which an equimolar quantity of tetrabutylammonium phosphate was dissolved, almost one-third of the liberated phosphate is in the form of pyrophosphate. In the *absence* of added phosphate, an even higher yield of pyrophosphate and condensed phosphorus acids is formed, as shown in Table I. Similarly,

TABLE I

YIELD OF INORGANIC PHOSPHATE AND CONDENSED PHOSPHATE IN DRY DMF

Quinol phosphate	Added substrate	% phosphate[c]	% condensed phosphate[d]
I[a]	None	52.5	47.5
I[b]	Bis(tetrabutylammonium) hydrogen phosphate	69	31
V[b]	Bis(tetrabutylammonium) hydrogen phosphate	68	32

[a] Bromine (0.8 ml.) was added to a dry DMF solution (50 ml.) of quinol phosphate (1.3 g.) at room temperature. After 1 hr., cyclohexene was added to absorb excess bromine; water was then added (50 ml.) and the organic matter was extracted with ether. A mixture of phosphates was precipitated from the aqueous layer with $BaCl_2$ at pH 7–8. [b] Experimental conditions as described above with addition of bis(tetrabutylammonium) phosphate (1.65 g.). Paper chromatography indicated that only phosphate and pyrophosphate are formed in the presence of added inorganic phosphate. [c] Analyzed colorimetrically by the method Fiske and Subbarow.[5] [d] Total phosphate analyzed colorimetrically after 20-min. hydrolysis at 100° and per cent condensed phosphates calculated by difference.

(1) V. M. Clark, G. W. Kirby, and A. R. Todd, *Nature*, **181**, 1650 (1958).

(2) K. J. M. Andrews, *J. Chem. Soc.*, 1808 (1961).

(3) V. M. Clark, D. W. Hutchinson, G. W. Kirby, and A. R. Todd, *ibid.*, 715 (1961).

(4) A. Lapidot and D. Samuel, *Biochim. Biophys. Acta*, **65**, 164 (1962).

Clark, *et al.*,[3] have found that in the breakdown of 2-methylnaphthalenediol 1,4-diphosphate[1] (Synkavit, V) under similar conditions, the product contains 50% orthophosphate, 15% pyrophosphate, and 35% trimetaphosphate. We have found in the presence of added phosphate in DMF solution that Synkavit (V) gives only phosphate and pyrophosphate (see Table I). It has also been reported[6] that when a quinol phosphate reacts in the presence of P^{32}-labeled inorganic phosphate, no radioactivity is detectable in the pyrophosphate, and that this observation rules out any simple nucleophilic attack by inorganic phosphate on metaphosphate. We have run the same reaction with both quinol monophosphate (I) and diphosphate (V) in the presence of O^{18}-labeled tetrabutylammonium phosphate and found that O^{18}-labeled pyrophosphate is formed in good yield.

These results are presented in Table II.

TABLE II

O^{18} IN PHOSPHATE AND PYROPHOSPHATE FROM OXIDATIVE HYDROLYSIS OF QUINOL PHOSPHATE IN DRY DMF[a]

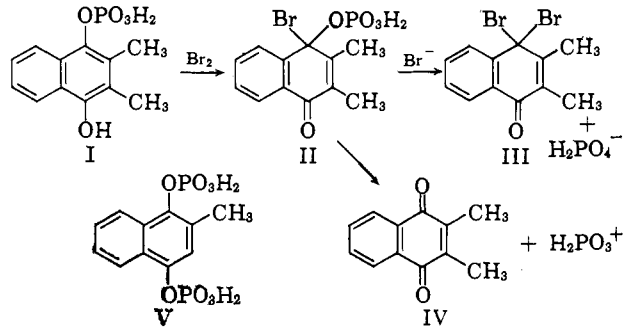
Quinol phosphate	Atom % excess O^{18} in added phosphate	Atom % excess O^{18} in product phosphate	Atom % excess O^{18} in product pyrophosphate[b]
I	11.1	5.1	3.9
V	21.4	12.8	8.0

[a] Conditions as in Table I. [b] Pyrophosphate isolated as zinc salt at pH 3–4. Oxygen isotopic analyses of phosphate and pyrophosphate by method of Anbar and Guttmann.[7]

It is apparent from Table II that O^{18} enrichment of the phosphate at the end of the reaction is considerably lower than at the start, indicating dilution by unlabeled inorganic phosphate. This phosphate must be formed in the course of the reaction, by C–O bond fission.

The O^{18}-enriched pyrophosphate in the product must be formed by phosphorylation of the total amount of inorganic phosphate by a "metaphosphate" intermediate formed by P–O bond fission. There appear, therefore, to be two parallel reaction pathways for the breakdown of a quinol phosphate in the presence of bromine in DMF solution, each involving bond fission in a different position.

The following tentative mechanism is suggested for the reactions of the monophosphate.



The quinonoid intermediate II which has not been isolated is similar to those suggested[8] for the bromination of phenols. The step converting II to III is a halide ion cleavage of an alkyl ester phosphate with attack on carbon similar to those found[9] for certain secondary and tertiary alkyl phosphates. Intermediate III has not been isolated since it is converted to the quinone IV on work-up. A quinonoid intermediate, the dimethyl ketal of *p*-benzoquinone, has been isolated by Durckheimer and Cohen[10] from the breakdown of hydroquinone phosphate in methanol solution, using ceric ammonium nitrate as oxidizer. In DMF solution the "metaphosphate" intermediate formed by P–O bond fission may be transiently bound to the solvent as an imidoyl phosphate. Enol phosphates of acid amides of this type have been prepared by Cramer.[11]

From the amount of pyrophosphate produced (see Table I) in the breakdown of compounds I and V, it appears that in DMF solution, the extent of P–O bond fission is about 30%. This is of the same order as the P–O bond fission of I in water.[4]

(5) C. H. Fiske and Y. Subbarow, *J. Biol. Chem.*, **66**, 375 (1925).
(6) G. E. Tomasi, J. W. Hamilton, and R. D. Dallam, *Federation Proc.*, **21**, 53 (1962).
(7) M. Anbar and S. Guttmann, *Intern. J. Appl. Radiation Isotopes*, **4**, 233 (1959).
(8) K. Fries and H. Engel, *Ann.*, **439**, 232 (1924); V. V. Ershowv and A. A. Volodkin, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 730 (1962).
(9) L. Zervas and I. Dilaris, *J. Am. Chem. Soc.*, **77**, 5354 (1955).
(10) W. Durckheimer and L. A. Cohen, *ibid.*, in press.
(11) F. Cramer, *Angew. Chem.*, **72**, 236 (1960).

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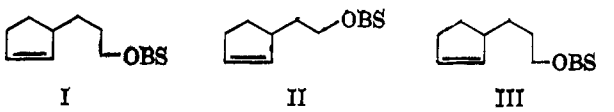
Ring Closure to the Bicyclooctyl System in the Solvolysis of 3-(Δ^2-Cyclopentenyl)propyl Brosylate[1,2]

Sir:

In recent years the investigation of cyclizations of unsaturated sulfonate esters under solvolytic conditions has been fruitful both from a theoretical and from a synthetic viewpoint. Confirming evidence for the unique stability of the 2-norbornyl cation was obtained from solvolytic studies on 2-(Δ^3-cyclopentenyl)ethyl sulfonates,[3] while similar studies have contributed evidence concerning nonclassical cations of the bicyclo[3.2.1]octyl and bicyclo[2.2.2]octyl systems.[4] Even the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate yielded interesting data concerning the character of the cyclohexyl carbonium ion.[5] In this communication we wish to describe some of our results concerning the solvolysis of 3-(Δ^2-cyclopentenyl)propyl brosylate (I) and the related compounds 2-(Δ^2-cyclopentenyl)ethyl brosylate (II) and 3-cyclopentylpropyl brosylate (III).



I II III

The alcohols corresponding to the brosylates were prepared by standard techniques and had properties

(1) Presented before the Organic Division at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.
(2) This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 1272-A4).
(3) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).
(4) (a) G. Le Ny, *Compt. rend.*, **251**, 1526 (1960); (b) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).
(5) P. D. Bartlett, *Ann.*, **653**, 45 (1962); P. D. Bartlett, W. D. Closson, and T. J. Cogdell, paper presented at the 100th Annual Meeting of the National Academy of Sciences, Washington, D. C., April, 1963.