

CCF_2CF_3 , but less readily than $\text{CF}_2=\text{CFCF}_2$ - $\text{CF}=\text{CF}_2$ owing to the accumulation of relatively stable intermediates.

The above results not only establish a new type of fluorolefin rearrangement but demonstrate the feasibility of carrying out fluoride ion reactions involving attack on unsaturated carbon in the absence of a solvent under heterogeneous conditions at moderate temperatures. This type of reaction technique with cesium fluoride will be of considerable value in overcoming some of the difficulties previously encountered in bringing about reactions of fluoride ion with carbon-fluorine compounds.²

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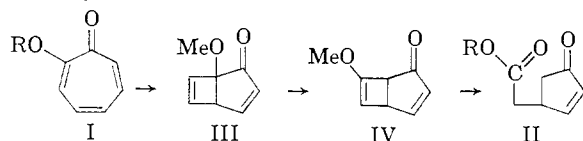
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PHOTOISOMERIZATIONS IN THE α -TROPOLONE SERIES: THE MECHANISTIC PATH OF THE α -TROPOLONE TO 4-OXO-2-CYCLOPENTENYLACETIC ACID CONVERSION

Sir:

It has been reported¹ that ultraviolet irradiation of an aqueous solution of α -tropolone (Ia) gives the acid IIa and more recently that a similar irradiation of tropolone methyl ether (Ib)^{2,3} gives the ester I Ib. Various mechanisms have been considered for these transformations¹⁻³ and we now present evidence which clearly defines the mechanistic pathway from I to II.



a, R = H; b, R = Me

Irradiation¹ of a methanolic solution of Ib in a Pyrex vessel gave photoisomers III (224 m μ , 5.82 μ) and IV (223 m μ , 5.84 μ), separated by vapor phase chromatography. Pyrolysis of III (440°) gave α -tropolone methyl ether (Ib), indicating only valence tautomeric changes, and pyrolysis of IV (420°) gave 3-methoxytropone⁴ (hydrobromide, m.p. 118°), indicating a rearrangement. Hydrogenation of IV over palladium-charcoal gave a tetrahydro derivative (5.75 μ ; 2,4-dinitrophenylhydrazone, m.p. 170–172°). The n.m.r. spectra of III (2.75 and 4.33 τ , β and α proton; 3.62 and 3.90 τ , cyclobutene protons; 6.40 τ , methoxyl proton; 6.74 τ , ring juncture proton) and of IV (2.42 and 4.07 τ , β and α proton; 5.07 τ , cyclobutene proton; 6.40 τ , ring juncture protons; 6.52 τ , methoxyl protons) clearly estab-

(1) W. G. Dauben, K. Koch and W. E. Thiessen, *J. Am. Chem. Soc.*, **81**, 6087 (1959).

(2) E. J. Forbes and R. A. Ripley, *Chem. and Ind. (London)*, 589 (1960).

(3) W. G. Dauben and K. Koch, Abstracts of International Symposium on Chemistry of Natural Products, Sydney, Australia, 1960, p. 51.

(4) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, 4605 (1954).

lished the assigned structures. IV upon irradiation in water or on treatment with dilute aqueous acid gave keto ester I Ib. The sequence I, III, IV, II for the reaction was established by v.p.c. analysis of aliquots removed during irradiation in methanol. As I decreased, III began to appear and more slowly IV was formed. Continued irradiation left only IV which after the addition of water decayed to II.

The nature of the shift of the methoxyl group was defined clearly by study of 4-methyl and 6-methyltropolone methyl ether. Under similar conditions, the 4-methyl isomer (Va) gave valence tautomer VIa (230 m μ , 5.85 μ) and subsequently rearranged to VIIa (226 m μ , 5.93 μ). The n.m.r. spectrum of the valence tautomer VIa shows a one-proton doublet at 3.80 τ (α -proton), a one-proton quartet at 2.36 τ (β -proton), a one-proton peak at 6.32 τ (bridgehead proton), a three-proton

peak at 8.12 τ ($\text{CH}_3-\text{C}=\text{C}-$), a one-proton peak at 4.07 τ (cyclobutene proton) and a three-proton peak at 6.58 τ (OCH_3). The rearranged photoproduct VIIa shows a pair of doublets at 4.34 and 2.55 τ (α - and β -protons), a three-proton singlet

at 8.60 τ ($\text{CH}_3-\text{C}-$), a one-proton peak at 5.07 τ

(cyclobutene proton), a three proton-peak at 6.45 τ (OCH_3) and a one-proton peak at 6.95 τ (bridgehead proton). The 6-methyl isomer Vb first went to VIb (229 m μ , 5.89 μ) and then to VIIb (223 m μ , 5.89 μ). The valence tautomer VIb shows peaks

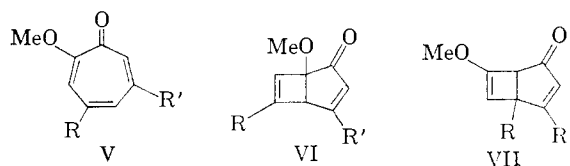
at 4.15 τ (α -proton), 7.88 τ ($\text{CH}_3-\text{C}=\text{C}-\text{C}=\text{O}$), 6.32 τ (bridgehead proton), 3.62 and 3.21 τ (cyclobutene protons) and 6.57 τ (OCH_3). The rearranged photoproduct VIIb shows peaks at 4.25

τ (α -proton), 7.94 τ ($\text{CH}_3-\text{C}=\text{C}-\text{C}=\text{O}$), 6.68 and 6.42 τ (bridgehead protons), 4.91 τ (cyclobutene hydrogen), and 6.33 τ (OCH_3). Both VIIa and VIIb upon acid treatment or irradiation in water yielded the ester analog of II. The ester X shows a pair of doublets at 4.00 and 2.43 τ (α - and β -protons), a three proton singlet at 8.70 τ

($\text{CH}_3-\text{C}-$), a two-proton singlet at 7.50 τ (methyl-

ene adjacent to the ester carbonyl), a peak at 6.37 τ ($-\text{OCH}_3$) and a pair of one-proton doublets at 7.65 and 7.84 τ (methylene adjacent to the ketone carbonyl).

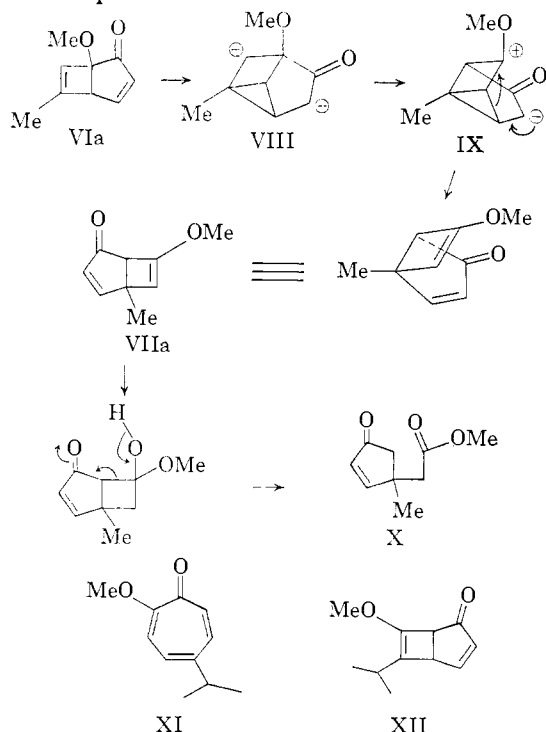
The direction of the shifts of the methyl and methoxyl in going from the tropolone structure to the bicyclic structure of type IV or VII can be accounted for in the following manner. The first step is the formation of the expected valence tauto-



a, R = CH₃, R' = H
b, R = H, R' = CH₃

meric structure (III or VI).⁵ In these latter structures the ultraviolet maximum is at a somewhat longer wave length than expected for a simple cyclopentenone. This bathochromic shift may be attributed to interaction between the non-conjugated double bond in the four-membered ring and the cyclopentenone chromophore,⁵ as indicated by excited state VIII. Light induced migration of the carbonyl carbon gives rise to excited state IX which can collapse to ground state VIIa. Hydrolysis of VIIa via the hemiketal leads directly to ester X. In accord with prediction based upon this mechanistic picture, irradiation of γ -thujaplicin methyl ether (XI) in methanol gave XII (other unidentified products are formed).

Satisfactory analyses have been obtained for all new compounds.



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(5) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

(6) National Science Foundation Cooperative Predoctoral Fellow, 1959-1961.

(7) National Institutes of Health Predoctoral Fellow, 1959-1961.

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HCP, A UNIQUE PHOSPHORUS COMPOUND

Sir:

We wish to report the first¹ successful synthesis of a trivalent phosphorus compound that unquestionably contains a multiple P-C bond.²

Methinophosphide (HCP) has been prepared by passing phosphine through a low intensity (50-100 amperes, 25 volts) rotating arc struck between graphite electrodes contained in a water-cooled copper reactor.³ The average operating pressure was 40 mm. and the gaseous products were quenched in traps maintained at -196° . In a typical arc experiment, 20 g. of PH_3 was treated in about one hour.⁴ The condensable volatile products, HCP and acetylene in 1:4 molar ratio with traces of phosphine and ethylene, were separated on a gas-chromatographic column (helium carrier gas, ethyl N,N-dimethyl oxalamate partition fluid, silica gel support). A large excess and fast throughput of helium were necessary to minimize loss of HCP through polymerization.

HCP is a very reactive colorless gas, stable to storage in the pure state only at temperatures below its triple point of $-124 \pm 2^{\circ}$. The vapor pressure at this temperature is approximately 30 mm. The monomer polymerizes slowly at -130° and more rapidly at -78° to a black solid. Both the monomer and the freshly formed polymer are extremely pyrophoric when exposed to air, even at low temperatures. However, on prolonged standing, the insoluble and infusible polymer becomes considerably less reactive.

Anal. Calcd. for $(\text{HCP})_x$: H, 2.27; C, 27.28; P, 70.45. Found: H, 2.95; C, 26.77; P, 71.07.

This establishes the empirical proportions of the monomer since no other products are formed in the polymerization.

There are two possible monomeric structures, $\text{H}-\text{C}\equiv\text{P}$ and $\text{H}-\text{P}\equiv\text{C}$, and numerous polymeric structures that can be assigned. Analysis of the mass spectrum of this compound out to 204 m./e. units lends strong support to a monomeric formulation, since no peaks at 88 (dimer) or 132 (trimer) were detectable. The data, however, do not distinguish between HCP and HPC structures because rearrangement, *i.e.*, hydrogen migration, is common in mass spectral analyses of unsaturated

m./e.	Rel. intensity	Assignment
45	1.3 (theor. 1.29) ⁵	HC_{12}P^+
44	100	HC_{12}P^+ , C_{13}P^+
43	16.7	C_{12}P^+
32	1.4	HP^+
31	12.1	P^+
22	4.0	$\text{HC}_{12}\text{P}^{++}$, $\text{C}_{13}\text{P}^{++}$
$15^{1/2}$	0.5	P^{++}
13	3.1	HC_{12}^+ , C_{13}^+
12	3.7	C_{12}

(1) The literature contains relatively few references to the carbon-phosphorus triple bond. W. B. Shober and F. W. Spanutius [*J. Am. Chem. Soc.*, **16**, 229-232 (1894)] claim a synthesis of NaCP, without analytical data, but their work could not be confirmed in this laboratory. H. Albers [*Angew. Chem.*, **62**, 443-467 (1950)] discusses the existence of HCP and HCAs.

(2) In ylides, R_2PCR_2 , the P-C bond certainly has multiple bond character but the ionic form is probably the major contributor to the ground state.

(3) The hollow cathode was positioned coaxially with a cup-shaped anode so that a conical arc curtain was maintained.

(4) Long operating times were precluded in our arc apparatus because of plugs of red and yellow phosphorus from thermal decomposition of PH_3 . This disproportionation accounted for the major portion of phosphorus values introduced into the reactor and resulted in very low yields of condensable off-gases (0.5-1.0 g.).

(5) This value is based on intensity of 44 peak for HC_{12}P^+ and C_{13}P^+ .