TABLE I

ALKYLATION OF METAL ENOLATE OF
2-CARBETHOXYCYCLOPENTANONE

Metal	Halide	Time, hr	Yield, %[a]	O-Alkylation, %[b]
K	$(CH_3)_2CHBr$	5	61	7
K	$(CH_3)_2CHI$	12	77	0
Na	$(CH_3)_2CHI$	3	78	15
K	$CH_3(CH_2)_2CH_2Br$	5	82	0
Na	$CH_3(CH_2)_2CH_2Br$	15	90	14
K	$c\text{-}C_6H_{11}Br$	11	40	~40
K	$BrCH_2CO_2Et$	1	94	0
K	$PhCH_2CH_2Br$	6	79	0

[a] Total yield of alkylated keto ester. [b] As per cent of total yield determined by glpc. Limit of detection <1%.

any O-alkylated product when the potassium salt was alkylated with isopropyl iodide. Use of isopropyl bromide, however, did result in some O-alkylation (see Table I).

Experimental Section[6]

The typical alkylation reaction is exemplified by the reaction described below.

2-(2-Phenylethyl)-2-carbethoxycyclopentanone.[7]—To 6.27 g (0.0268 mole) of the potassium salt of carbethoxycyclopentanone[8] in 50 ml of dry dimethyl sulfoxide was added dropwise 8.70 g (0.0536 mole) of freshly distilled 1-bromo-2-phenylethane. The resulting solution was allowed to stir at room temperature under a nitrogen atmosphere. After 6 hr, the reaction mixture was poured into water and extracted with pentane. The pentane extract was washed with water and dried over magnesium sulfate. Distillation afforded 5.27 g (78.8%) of 2-(2-phenylethyl)-2-carbethoxycyclopentanone, bp 90° (oil bath) at 0.1 torr.

2-(2-Phenylethyl)cyclopentanone.—A solution of 2.604 g (0.0103 mole) of 2-(2-phenylethyl)-2-carbethoxycyclopentanone in 100 ml of 3 N hydrochloric acid was refluxed for 24 hr. The reaction mixture was then poured into water and extracted several times with pentane. The pentane extracts were combined, washed with 10% sodium bicarbonate solution and then with water, and dried over magnesium sulfate. Distillation afforded 1.52 g (78.5%) of 2-(2-phenylethyl)cyclopentanone, bp 125° (oil bath) at 0.2 torr.

Registry No.—2-Carbethoxycyclopentanone, 611-10-9; dimethyl sulfoxide, 67-68-5; 2-(2-phenylethyl)-2-carbethoxycyclopentanone, 14721-43-8; 2-(2-phenylethyl)cyclopentanone, 14721-44-9.

(6) The dimethyl sulfoxide was distilled from calcium hydride. Identification of products was based upon comparison of nuclear magnetic resonance and infrared spectra with those of the known 2-alkylcyclopentanones obtained by hydrolysis and decarboxylation, and, in appropriate cases, of the alkylated esters. We wish to thank the National Science Foundation for funds toward the purchase of a Varian A-60 nmr spectrometer and Crown Zellerbach Corp., Camas, Wash., for a generous gift of dimethyl sulfoxide.

(7) H. Adkins and G. F. Hager, J. Am. Chem. Soc., 71, 2965 (1949).

(8) R. Mayer, G. Wenschuh, and W. Topfelmann, Chem. Ber., 91, 1616 (1958). The commercial mixture of methyl and ethyl esters was used.

Transannular Aldol Condensation of Cyclododecane-1,6-dione and Cyclododecane-1,7-dione

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Cyclododecane-1,6-dione[1] and cyclododecane-1,7-dione have become readily available from the microbiological oxygenation of cyclododecanol.[2] Both

(1) E. T. Niles and H. R. Snyder, J. Org. Chem., 26, 330 (1961).

diketones undergo ready transannular aldol condensation comparable to that reported for cyclodecane-1,6-dione.[3] Treatment of cyclododecane-1,7-dione with aqueous methanolic potassium carbonate at room temperature gave a 66% yield of 8-hydroxybicyclo[6.4.0]dodecan-2-one. The same condensation carried out under more vigorous conditions with sodium methoxide gave less pure product contaminated with a conjugated keto compound, presumably bicyclo[6.4.0]dodec-1(8)-en-2-one.

Treatment of cyclododecane-1,6-dione with methanolic sodium methoxide gave a mixture of three unsaturated ketones, one of which was nonconjugated and the others conjugated. Wolff–Kishner reduction of the mixture, followed by ozonolysis, afforded cyclododecane-1,7-dione and cyclododecane-1,5-dione,[2] suggesting that the structures of the two conjugated ketones are probably bicyclo[5.5.0]dodec-1(7)-en-2-one and bicyclo[7.3.0]dodec-1(9)-en-2-one. The third (nonconjugated) ketone is assumed to be a β,γ-unsaturated isomer of one of the conjugated ketones.

Experimental Section[4]

8-Hydroxybicyclo[6.4.0]dodecan-2-one.—Two grams of cyclododecane-1,7-dione dissolved in 100 ml of methanol and 20 ml of 10% potassium carbonate solution was allowed to stand in a covered beaker for 44 hr. The mixture was adjusted to pH 6–7 with 1 N hydrochloric acid and solvent was allowed to evaporate at room temperature to a final volume of 25–30 ml. After chilling at 0–5° the product was recovered and washed with cold water; yield 1.32 g, mp 70–71°. The infrared spectrum showed an extremely sharp hydroxyl absorption at 3500 and carbonyl absorption at 1685 cm⁻¹. Recrystallization from pentane did not change the melting point.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.56; H, 10.33.

When a solution of 0.30 g of cyclododecane-1,7-dione in 6 ml of methanol was heated on a steam bath for 10 to 135 min with 0.15 g of sodium methoxide, approximately 0.25 g of crude crystalline 8-hydroxy-bicyclo[6.4.0]dodecan-2-one, mp 52–58°, was obtained which showed a trace of ultraviolet absorption at 250 mμ and a weak infrared absorption (shoulder) at 1675 cm⁻¹, perhaps due to a trace of dehydration product.

Attempts to prepare the dehydration product by treating the 8-hydroxybicyclo[6.4.0]dodecan-2-one with p-toluenesulfonic acid resulted, even after a 3.5-hr reflux in benzene through a Dean–Stark trap, only in low conversions (λ_{max} 251 mμ (ϵ 4720)) to conjugated ketone.

Aldol Condensation of Cyclododecane-1,6-dione.—This condensation was conducted with sodium methoxide as described above for the 1,7-dione to give a mixture of (probably) bicyclo[5.5.0]dodec-1(7)-en-2-one, bicyclo[7.3.0]dodec-1(9)-en-2-one, and a nonconjugated ketone. The infrared spectrum had maxima at 1710 (nonconjugated C=O), 1665, 1648 (conjugated C=O), and 1628 cm⁻¹ (C=C).

The semicarbazone of the mixed ketones was prepared in the usual manner by heating the mixture at reflux with semicarbazide hydrochloride and sodium acetate in aqueous methanol. The twice recrystallized product melted at 192–195°; λ_{max}^{EtOH} 269 mμ (ϵ 19,850).

Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.29; H, 8.87; N, 17.52.

Hydrolysis of this semicarbazone with aqueous methanolic sulfuric acid gave a ketonic mixture with an infrared spectrum as described above.

Wolff–Kishner Reduction.—The aldol condensation product obtained from 1.88 g of 1,6-cyclododecanedione was refluxed for 1 hr with 15.0 ml of triethylene glycol, 1.5 ml of 99% hydra-

(2) G. S. Fonken, M. E. Herr, H. C. Murray, and L. M. Reineke, J. Am. Chem. Soc., 89, 672 (1967).

(3) W. Hückel, R. Danneel, A. Schwartz, and A. Gercke, Ann., 474, 121 (1930); W. Hückel, A. Gercke, and A. Gross, Ber., 66, 563 (1933).

(4) Melting points were determined using a Fisher-Johns block. Florisil is a synthetic magnesium silicate product of the Floridin Co., Warren, Pa.

zine hydrate, and 2.0 g of potassium hydroxide and then heated under a water takeoff trap until the temperature of the mixture was 175°. Refluxing was continued for 3 hr. The mixture was cooled and combined with the liquid in the water trap, diluted with water, and extracted with ether. The extract was washed with dilute sulfuric acid and water and dried (sodium sulfate) and the solvent removed to give a yellow oily hydrocarbon mixture which showed no carbonyl absorption in the infrared.

Ozonization.—The hydrocarbon mixture was dissolved in 150 ml of methylene chloride and kept at −5 to −10° while a stream of ozone–oxygen was passed through the solution for 70 min at the rate of about 20 mg of ozone per minute. The solvent was removed under reduced pressure at room temperature. The residue was taken up in 25 ml of acetic acid and mixed with 4.0 g of zinc dust for 5 min. The zinc residue was removed by filtration and washed with ether, and the combined filtrate–wash was made basic with saturated potassium carbonate solution. The ether extract was washed with water and dried and the solvent removed to give a colored oil which appeared to be decomposing and darkening due to ozonide remaining in the mixture; it was again treated with zinc dust and acetic acid for 30 min and worked up as described above. The resulting oil in 25 ml of benzene was chromatographed over Florisil as described earlier[2] to give cyclododecane-1,7-dione, mp 129–133°. The infrared spectrum and paper chromatographic behavior were identical with authentic material.

Paper chromatographic analyses[5] of the appropriate eluate indicated the presence of cyclododecane-1,5-dione.[2]

(5) We are indebted to Mr. L. M. Reineke for these analyses.

Syntheses of Substituted Phosphetanes and Related Derivatives

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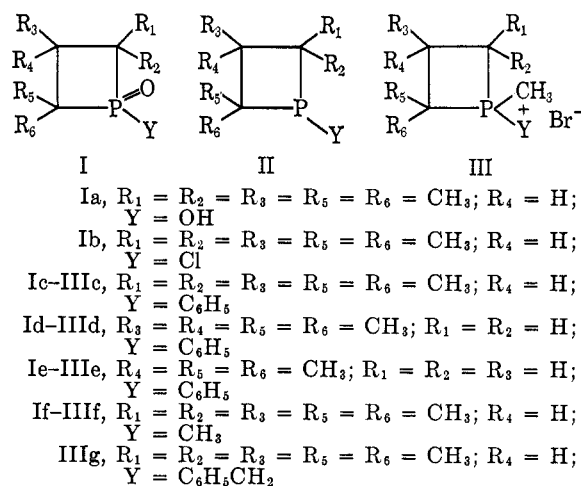
In the initiation of a general program designed to explore the syntheses, chemical reactions, and physical properties of small-membered ring phosphorus heterocycles, we were prompted to investigate further the previously reported[1] synthesis of 1,1,2,3,3-pentamethyltrimethylenephosphinic acid (Ia) and the acid chloride (Ib). These compounds, which were prepared by treatment of 2,4,4-trimethyl-2-pentene (IV) with phosphorus trichloride in the presence of aluminum chloride, represent one of the few known cases[2] of a four-membered ring containing a single phosphorus heteroatom.

We have now found that treatment of IV with the preformed complex from phenylphosphonous dichloride (V) and aluminum chloride afforded 2,2,3,4,4-pentamethyl-1-phenylphosphetane 1-oxide (Ic) in moderate yield and that similar treatment using methylphosphonous dichloride produced If. Although it was possible to prepare Ic from Ib by treatment with phenyllithium, the yield was low due to the subsequent, rapid reaction of Ic with phenyllithium to give an open-chain compound.[3]

(1) (a) J. J. McBride, Jr., E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, **27**, 1833 (1962); (b) E. Jungermann, J. J. McBride, Jr., R. Clutter, and A. Mais, *ibid.*, **27**, 606 (1962).

(2) (a) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957); (b) M. Green, *ibid.*, 541 (1965); (c) R. I. Wagner, U. S. Patent 3,086,053 (1963); *Chem. Abstr.*, **59**, 10124 (1963); U. S. Patent 3,086,056 (1963); *Chem. Abstr.*, **60**, 559 (1964).

(3) The structure of this compound will be the subject of a future report. There are a number of recorded examples of the reaction of phosphine oxides

Ia, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = OH$
Ib, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = Cl$
Ic–IIIc, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = C_6H_5$
Id–IIId, $R_3 = R_4 = R_5 = R_6 = CH_3$; $R_1 = R_2 = H$; $Y = C_6H_5$
Ie–IIIe, $R_4 = R_5 = R_6 = CH_3$; $R_1 = R_2 = R_3 = H$; $Y = C_6H_5$
If–IIIf, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = CH_3$
IIIg, $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$; $Y = C_6H_5CH_2$

Variation of the olefinic substrate was also investigated. Indeed, reaction of 2,3,3-trimethyl-1-butene (VI) with V and aluminum chloride afforded the crystalline product Id; and both 3,3-dimethyl-1-butene (VII) and 2,3-dimethyl-1-butene (VIII) reacted with V to give the *same* crystalline adduct Ie. The fact that VII and VIII produced the identical substance is consistent with the carbonium ion rearrangement proposed by McBride and co-workers.[1a] The former olefin underwent a methyl migration, whereas the latter olefin proceeded *via* a hydrogen migration to give the same intermediate species IX which can cyclize and subsequently lead to the observed phosphetane 1-oxide after hydrolysis.

IX
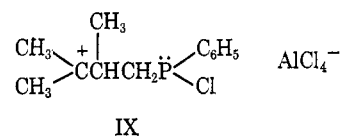
Support for the structures Ic–f comes from the corresponding nuclear magnetic resonance (nmr) spectra. Compound Id can be used to illustrate a typical analysis. The nmr ($CDCl_3$) shows each of the unequivalent methyl groups (R_5 and R_6) as a doublet centered at τ 8.62 and 9.07 with $^3J_{PCCH} = 17.5$ and 20.0 cps, respectively; each of the unequivalent methyl substituents (R_3 and R_4) occurs as a singlet at τ 8.72 and 9.00. The further assignment of which methyl is *cis* or *trans* relative to the phenyl group cannot be unambiguously made at this time. Finally, the two protons R_1 and R_2 show up as an ABX pattern (A = R_1; B = R_2; X = P^{31}) consisting of eight distinct absorption peaks (τ 6.90–7.92) with $^2J_{AB} = 15.0$ cps, $^2J_{PCH_A} = 17.0$ cps, and $^2J_{PCH_B} = 9.5$ cps; aromatic absorption appears in the region τ 1.97–2.68.

The nmr data were also useful in determining the proportion of geometric isomers which can exist in system Ic. R_3 can be either *cis* or *trans* relative to the phenyl group. For example, a mixture with a melting point range of 104–110° consisted of a 17:3 ratio of isomers (lower melting isomer:higher melting isomer). This ratio was readily obtained from the relative area of the peaks which were unique to each isomer and did not overlap. It was noteworthy that slow addition of water to the reaction mixture (quenching stage) gave a mixture (mp 117–125°) which consisted of

with organometallic reagents: D. Seyferth, *et al.*, *J. Am. Chem. Soc.*, **86**, 1100 (1964); D. Seyferth and D. E. Welch, *J. Organometal. Chem.* (Amsterdam), **2**, 1 (1964); G. Wittig and R. Rieber, *Ann.*, **562**, 187 (1949).