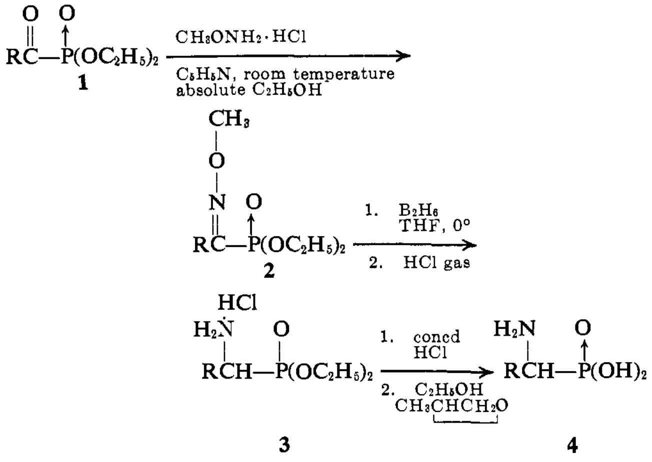
Route A



mum of alcohol and treatment of the solution with propylene oxide result in the precipitation of **4**. Table I contains pertinent data for the conversion of **1** → **2** → **3** → **4**. It appears that good confirmation of structure for most of the α-aminoalkylphosphonic acids in the literature is meager or totally lacking.

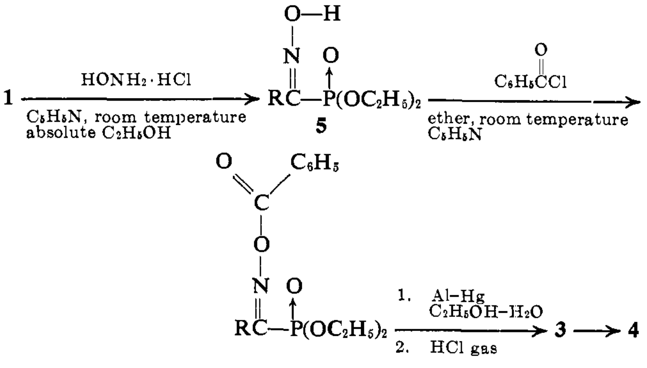
Table I. Conversion of $\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2}$ (**1**) → **2** → **3** → **4**

R	**2** Bp, °C (mm)	**3** Mp, °C	**4** Mp, °C	Yields, % 1 → 2	 2 → 3	 3 → 4
CH_3	80 (1.2)	Liquid[a]	278	83	56	96
CH_3CH_2	85 (1.0)	Liquid[a]	271	80	55	96
$CH_3(CH_2)_2$	80 (0.5)	135	276	84	57	96
$CH_3(CH_2)_3$	100 (1.3)	122	277	80	56	95
$(CH_3)_2CH$	76 (0.5)	116	274	80	57	96
$(CH_3)_2CHCH_2$	98 (0.5)	134	279	80	56	95
$CH_3CH_2C(CH_3)H$	75 (0.15)	129	274	80	58	95

[a] These amine hydrochlorides did not crystallize upon standing at 0° for 1 week. They were converted to the corresponding acid without further purification.

Starting from **1**, each member of **3** and **4** could be synthesized *via* the alternative route B, but the overall yields of **3** and **4** were always lower by 10–20%.

Route B



Mixture melting point determinations, and ir and nmr spectra confirmed the identity of each compound in **3** and **4**. Table II contains ^{31}P nmr data not previously recorded for some members of **3** and **4**. The crude oximes **5** and crude esters **6** were used in the scheme without purification.

Table II. ^{31}P Data for α-Aminoalkyl- and α-Aminoarylphosphonic Acids and the Hydrochloride Salts of the Diethyl Esters

$NH_3^+Cl^-$ | $RCHPO_3Et_2$, R =	Chemical shift, ppm[a]	NH_2 | $RCHPO_3H_2$, R =	Chemical shift, ppm[b]
$(CH_3)_2CH$	−21.26	CH_3	−17.62
$CH_3CH_2C(CH_3)H$	−21.34	$(CH_3)_2CH$	−16.36
C_6H_5	−17.5; $J = 8.4$ cps	$(CH_3)_2CHCH_2$	−18.13
p-$CH_3OC_6H_4$	−18.2; $J = 8.1$ cps	p-$CH_3OC_6H_4$	−13.33
p-$(CH_3)_3CC_6H_4$	−17.35; $J = 8.4$ cps		

[a] Measured in H_2O from the external standard of 85% H_3PO_4. [b] These compounds were dissolved in 85% H_3PO_4, and the spectrum was obtained quickly. Only the chemical shifts could be measured, since the viscous solutions were obtained and precluded enough resolution to see splitting patterns. Dilution with H_2O caused precipitation. Unfortunately, the acids were not sufficiently soluble in other solvents to obtain ^{31}P spectra or chemical shifts.

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The Tri-*t*-butylcyclopropenyl Cation

Sir:

We wish to report the first synthesis of the tri-*t*-butylcyclopropenyl cation *via* di-*t*-butylcyclopropenone. Reaction of α,α′-dibromodineopentyl ketone with potassium *t*-butoxide in tetrahydrofuran afforded, after sublimation of the crude product at reduced pressure, cyclopropenone I[1–3] in 35–40% yield, mp 61.5–62°. *Anal.* Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.45; H, 10.82. With the exception of the parent ion peak at *m/e* 166 the mass spectrum is very similar to that of di-*t*-butylacetylene. The infrared spectrum (CCl_4 solution) shows bands at 2980 (s), 2945 (m), 2920 (m), 2880 (m), 1875 (m), 1855 (s), 1820 (s), 1640 (s), 1485 (m), 1465 (m), and 1375 cm^{-1} (m). In addition to strong end absorption, I (in 95% EtOH) exhibited the characteristic $n \rightarrow \pi^*$ absorption of cyclopropenones in the ultraviolet at 260 mμ (ε 45.5).[1b,4,5]

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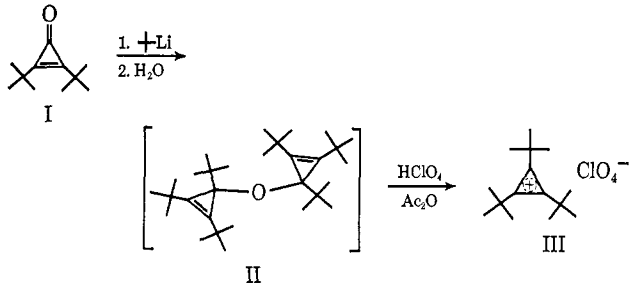
(1) The method employed was essentially that of Breslow: (a) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, 87, 1320 (1965); (b) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, 87, 1326 (1965).

(2) Professor F. D. Greene has kindly informed us that he has also prepared di-*t*-butylcyclopropenone by the same pathway.

(3) Compound I can also be prepared in very low yield by the reaction of di-*t*-butylacetylene with sodium trichloroacetate in refluxing dimethoxyethane followed by aqueous hydrolysis.

Nmr spectra of I (in $CDCl_3$) show a sharp singlet at δ 1.34.[6] Catalytic hydrogenation (Pt, dioxane) afforded dineopentyl ketone.[1] The remarkable stability of I can be demonstrated by its recovery in 86% yield (after sublimation) from treatment with a solution of 25% aqueous sodium hydroxide at reflux for 2 hr! Dipropylcyclopropenone, however, is completely destroyed under identical conditions.



Reaction of I with *t*-butyllithium in benzene afforded, after work-up with cold aqueous KH_2PO_4, an oil exhibiting characteristic cyclopropene absorption at 1820 cm^{-1} in the infrared, presumably due to bis(tri-*t*-butylcyclopropenyl) ether (II).[1a] Treatment of an ether solution of II with a 10% solution of perchloric acid in acetic anhydride resulted in the immediate precipitation of III as a white solid in 36–57% yield. Recrystallization from acetone gave white needles which decompose explosively at 248–250°. *Anal.* Calcd for $C_{15}H_{27}ClO_4$: C, 58.73; H, 8.87; Cl, 11.56. Found: C, 58.65; H, 8.74; Cl, 11.54. Compound III has infrared absorption (KBr) at 2980 (s), 2950 (m), 2920 (m), 2880 (m), 1485 (s), 1465 (s), 1425 (m), 1370 (s), 1225 (s), 1198 (s), 1090 (vs), 941 (w), 860 (m), and 626 cm^{-1} (s). Cation III (in CH_3CN) exhibits only end absorption in the ultraviolet as expected for alkyl-substituted cyclopropenyl cations.[4,7] The nmr spectrum (in $CDCl_3$) shows only a sharp singlet at δ 1.58 with the anticipated downfield shift of the *t*-butyl signal relative to the signal of I.

Potentiometric titration of cation III in 50% aqueous acetonitrile with 0.104 *N* NaOH gives a classical titration curve from which an apparent pK_{R^+} value of 6.6 is obtained. We have observed a pK_{R^+} of 7.0 for the tri-*n*-propylcyclopropenyl cation (IV) under identical conditions.[8]

In view of the greater electron-releasing inductive effect of *t*-butyl relative to the *n*-propyl substituent,[9] greater stability would be expected for cation III relative to IV.[7] Furthermore, steric considerations predict greater destabilization of the tri-*t*-butylcyclopropenyl alcohol relative to the tripropylcyclopropenyl alcohol. These two factors would predict a greater pK_{R^+} for III relative to IV, contrary to the observed results. On the other hand, solvation of charge would be more difficult in the hindered cation III relative to IV and may well be playing an important role.[10]

Acknowledgment. Generous support of this work by the National Institutes of Health (Grant No. GM 14579-02) is gratefully acknowledged.

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(4) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, 4, 10 (1965).

(5) We have observed the n → π^* transition of dipropylcyclopropenone (in 95% EtOH) at 252 mμ (ϵ 52.4).

(6) The Varian A-60A nmr spectrometer and the Hitachi RMU-6D mass spectrometer employed in this work were purchased through a National Science Foundation grant to Brown University.

(7) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

(8) The conditions employed for both pK_{R^+} determinations were identical with those previously described for IV. The reported pK_{R^+} of IV is 7.2 (see ref 7).

(9) (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press Co., New York, N. Y., 1962, p 9; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).

(10) (a) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961); (b) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); (c) for a good discussion of carbonium ions see D. Bethell and V. Gold, "Carbonium Ions," Academic Press Inc., New York, N. Y., 1967.

(11) National Aeronautics and Space Administration Trainee.

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Synthesis and Reactivity of Chloromethyl Phenyl Sulfoxide[1]

Sir:

We communicate in this report a new synthesis of chloromethyl phenyl sulfoxide,[2] $PhSOCH_2Cl$, and its resistance to bimolecular nucleophilic displacement reactions.

Although it is known that acylating reagents such as acyl anhydrides[3a] or acyl chlorides[3b] react with methyl sulfoxides, $RSOCH_3$, to give α-substituted methyl sulfides such as $RSCH_2OCOR$ or $RSCH_2Cl$, respectively, we have found that in the presence of pyridine *p*-toluenesulfonyl chloride reacts with methyl phenyl sulfoxide to yield chloromethyl phenyl sulfoxide without cleavage of the S–O bond. In the absence of pyridine this reaction gives almost exclusively chloromethyl phenyl sulfide. Attempted synthesis of chloromethyl phenyl sulfoxide by oxidation of chloromethyl phenyl sulfide failed.

In a typical experiment 28 g (0.2 mol) of methyl phenyl sulfoxide was added dropwise into a solution of *p*-toluenesulfonyl chloride (0.18 mol) in pyridine (0.4 mol) during 1 hr at 40–45°. After being acidified with cold dilute hydrochloric acid, the mixture was extracted thoroughly with *n*-hexane from which some chloromethyl phenyl sulfide and methyl phenyl sulfide was obtained. The aqueous layer was extracted thrice with chloroform; the combined extracts were washed once with water, dried with sodium sulfate, and fractionally distilled yielding 8.1 g (23%) of chloromethyl phenyl sulfoxide as a colorless viscous oil, bp 120–121° (4 mm). *Anal.* Calcd for C_7H_7SOCl: C, 48.14; H, 4.04; S, 18.36; Cl, 20.30. Found: C, 48.09; H, 4.11; S, 18.30; Cl, 20.42. The proton nmr spectrum of this compound shows a multiplet centered at τ 2.45 (aromatic protons) and a singlet at τ 5.61 (methylene protons), relative peak areas being 5:2. The infrared spectrum showed strong absorption at 1047 cm^{-1}, characteristic of sulfoxides. This compound is readily soluble in water and can be converted quantitatively by potassium permanganate into chloromethyl phenyl sulfone, mp 52°, lit.[4] mp 52–53°.

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(1) Presented at the 21st National Meeting of the Chemical Society of Japan, Osaka, Japan, March 31, 1968, Abstracts III, p 2037.

(2) F. G. Bordwell and W. T. Brannen, Jr., *J. Am. Chem. Soc.*, **86**, 4645 (1964).

(3) (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); (b) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, 77, 572 (1955).

(4) R. Otto, *J. Prakt. Chem.*, [2] 40, 527 (1889).