IX. Infrared absorption bands were found as follows: three broad peaks at 2900 (vs), 2660 (s), 2570 (s); two broad peaks at 1710 (vs) and 1680 (vs); 1460 (s), 1410 (s), 1380 (m), 1300 (vs), 1280 (m), 1255 (w), 1245 (w), 1220 (vw), 1205 (s), 1125 (w), 1095 (w), 1075 (w), 1040 (w), 1030 (vw), 948 (w); two broad peaks at 918 (vs) and 908 (vs); 825 (w), 808 (m), 784 (s), 748 (vw), 732 (m), 720 (vw), and 676 (s) cm.$^{-1}$.

The n.m.r. spectrum of IX was observed in acetone, water, and deuterium oxide at 60 Mc. and chemical shifts were recorded in parts per million relative to TMS. In deuterium oxide a water peak due to exchange of carboxylic acid protons was observed at 4.88 p.p.m. The end-cyclobutane-ring methylene hydrogens were observed as a sharp singlet at 2.67 p.p.m., area ratio corresponding to eight hydrogens. The center-cyclobutane-ring methylene hydrogens were observed as a sharp singlet at 2.21 p.p.m., area ratio corresponding to four hydrogens. In acetone-d_6 the n.m.r. spectra of IX had three peaks occurring at approximately 8.3, 2.7, and 2.2 p.p.m. in a ratio of 1:2:1 (4:8:4) corresponding to carboxyl hydrogens, end-ring methylene hydrogens, and center-ring methylene hydrogens.

The anilide of IX prepared directly from the reaction of aniline and IX at 180° had m.p. 212.2–213.0° when recrystallized twice from ethanol–water. The analysis indicated that decarboxylation of IX had occurred and that the derivative was the dianilide of dispiro[3.1.3.1]decanedicarboxylic acid (I).

Anal. Calcd. for $C_{38}H_{36}N_4O_4$, the tetraanilide of IX: C, 74.49; H, 5.92; N, 9.14. Calcd. for $C_{24}H_{26}O_2N_4$, the dianilide of I: C, 76.9; H, 7.03; N, 7.48. Found: C, 77.60; H, 7.18, N, 7.52.

cis- and *trans*-**Dispiro[3.1.3.1]decanedicarboxylic Acids (I).**—The title acids, I, were initially obtained as a mixture of the *cis* and *trans* isomers by thermal balance decarboxylation of dispiro-[3.1.3.1]decanetetracarboxylic acids (IX) as described above for the characterization of IX. Synthesis of I on a preparative scale was carried out in a semimicro sublimation apparatus with an internal cold finger. Tetraacid IX (400 mg., 1.28 mmoles) was put into the sublimer and the system was flushed with dry nitrogen. The sublimer was heated 10 min. in an oil bath at 220° after which time gas evolution ceased. The pressure on the system was gradually reduced to 1 mm. at which pressure white product I rapidly sublimed. The sublimate amounted to 272 mg. (1.21 mmoles, 94.5%), m.p. 174–175° (softening at 171°). Recrystallization from water did not raise the melting point.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 63.87; H, 7.15. Found: C, 64.27; H, 7.19.

The infrared spectrum of diacid I was observed in a potassium bromide pellet. The spectrum of I was clearly that of a carboxylic acid and was greatly simplified from the spectrum of the precursor of I, the tetraacid IX. The simplification in the spectrum is presumably due to absence of intramolecular hydrogen bonds in I relative to IX. The infrared spectrum of I had absorption bands as follows: 3310 (m), 2940 (w), 2860 (s), 2780 (w), 2690 (w), 2595 (w), 2520 (w), 1692 (vs), 1450 (w), 1410 (s), 1330 (m), 1257 (s), 1245 (w), 1207 (w), 1177 (w), 1115 (broad, w), 1043 (w), 1020 (w), 858 (broad, w), 807 (broad, w), 757 (m), and 727 (w) cm.$^{-1}$.

The 60-Mc.p.s. n.m.r. spectrum of the sodium salt of I in deuterium oxide solution is shown as Figure 1. The spectrum of I is interpreted to be in agreement with the structure assigned.

2-8-Dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 Acid (I-D).—N.m.r. spectra of 2,2,8,8-dispiro[3.1.3.1]decanedicarboxylic acid (IX) were observed in deuterium oxide solution. Recovery of IX and further equilibration with deuterium oxide gave IX tetrasubstituted by deuterium at the carbonyl groups of IX. Decarboxylation of tetradeuterated IX (2,2,8,8-dispiro[3.1.3.1]-decanedicarboxylic acid-d_4) by the procedure described above for I gave 2,8-dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 acid (I-D). The 60-Mc.p.s. n.m.r. spectrum of the sodium salt of I-D is shown in Figure 2.

Acknowledgment.—The authors wish to thank the San Diego State College Foundation for partial support of this research.

Additions of a Phosphorane to Dimethyl Acetylenedicarboxylate

JAMES B. HENDRICKSON,[1] CALVIN HALL, RICHARD REES, AND JOHN F. TEMPLETON

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02145

Received May 10, 1965

Triphenylphosphorylideneacetophenone forms two adducts with dimethyl acetylenedicarboxylate, one in methanol (protic solvent) involving a simple *trans* Michael addition (**3**), the other in dry ether (aprotic solvent) involving a four-membered phosphorane ring intermediate and thus a 1,3 shift of the triphenylphosphorus group, in effect **10**. An isomer (**7**) of the first adduct, formed in acid, and other chemical transformations of the two are described, including chemical and physical evidence in confirmation of the assigned structures. A rationalization of the preference for four-centered intermediates involving phosphorus is presented, and the various adducts are shown to conform to the expected modes of additions to acetylenedicarboxylate.

In connection with studies on the preparation and properties of phosphoranes with five single P–C bonds, we considered the possibility of a Diels–Alder reaction between a dienophile and a ketophosphorane such as **1**. When triphenylphosphorylideneacetophenone (**1**) was boiled in methanol with dimethyl acetylenedicarboxylate, a pale yellow crystalline product was, in fact, formed. The empirical composition and physical properties were consistent with its formulation[2] as the expected adduct 2 (see Chart I), as was the formation on bromination of a monobromo compound of very similar properties. The infrared spectra of the two compounds showed the conjugated ester absorption of 5.83 μ and bands at 6.2, 6.3, 6.6, and 6.95 μ assigned to olefinic and aromatic absorptions. The n.m.r. spectrum of the adduct showed two ester methoxyl singlets of three protons each at τ 6.67 and 6.97, a complex multiplet of 20 protons at τ 2–3, and a single proton as a doublet (J = 3 c.p.s.)[3] at τ 4.81 which disappeared on bromination.

Our concurrent experiments with the nature of additions to acetylenedicarboxylate esters,[5] however, suggested another formulation in the isomeric *trans* Michael adduct **3**. Pyrolysis of the adduct led to quantitative yields of triphenylphosphine oxide and the acetylenic ester **4** identified by analysis, infrared absorptions at 4.49 ($C\equiv C$), 5.78 ($COOCH_3$), and 6.20 μ ($C{=}C$), and hydrogenation and saponification to the known[6] β-phenylethylsuccinic acid, which formed

---

[1] Alfred P. Sloan Foundation Fellow.

[2] Reported in a preliminary communication: J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 2018 (1961).

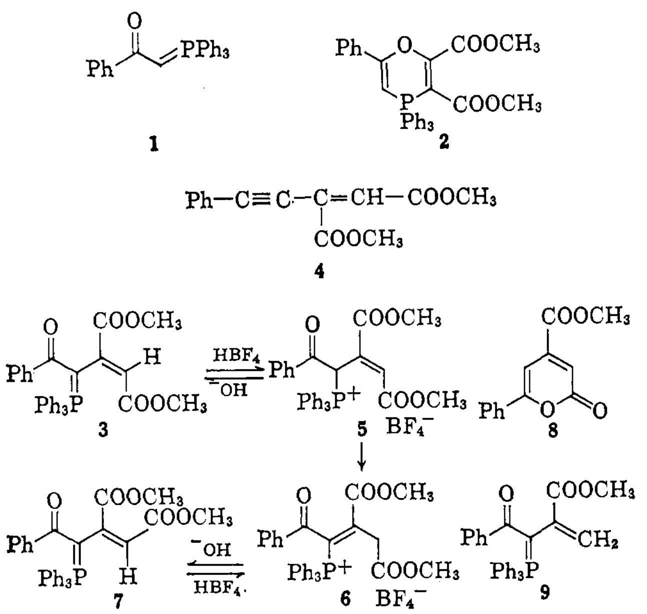
[3] The splitting of the proton signal by the proximate phosphorus nucleus led us to explore a series of phosphorus compounds as models.[4]

[4] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

[5] J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Am. Chem. Soc.*, **86**, 107 (1964).

[6] J. Thiele and J. Meisenheimer, *Ann.*, **306**, 247 (1899).

CHART I



an oily five-membered anhydride (infrared absorptions at 5.38 and 5.58 μ) on pyrolysis. This product bears the complete carbon skeleton of **3**, but not of **2**, and the pyrolysis reaction was completely analogous to the pyrolytic conversions of ketophosphoranes into acetylenes later reported by Trippett,[7] who independently suggested the formula **3** for the adduct. The spectra are also consistent with **3**, the intense infrared band at 6.62 μ being assigned to the very considerably conjugated ketone group which absorbs at the same position in the model (**1**).

The adduct was mildly basic: when a pale yellow solution in methylene chloride was shaken with aqueous HBF$_4$, it went colorless immediately and evaporation of the organic solvent led to a colorless oil with a new infrared spectrum exhibiting fairly strong bands at 6.00 and 6.28 μ in place of the 6.62-μ carbonyl of the initial adduct as well as intense absorption in the 9–10-μ region, typical of BF$_4^-$. When the oil is made basic directly, a quantitative yield of the initial yellow adduct is returned. However, dissolved in wet ether and allowed to stand, the oily salt slowly deposits colorless crystals with the composition of a monofluoroborate of **3** and different absorption in the infrared, *viz.*, no 6.0-μ band but a less intense group at 6.10–6.25 μ (the 5.8- and 9–10-μ absorptions were present in both salts). Addition of alkali to a solution of this second salt led immediately to a yellow color and quantitative production of an orange crystalline isomer of the original adduct (**3**) having very similar properties. Analogous acidification of this isomer with HBF$_4$ led immediately to the crystalline salt only. Short boiling of an acidified methanolic solution of the original adduct and basification also cleanly yielded the new isomer, which is formulated as the geometrical isomer **7**.

These results are consistent with expectation, for, if adduct **3** is initially formed by *trans* addition of **1** to methyl acetylenedicarboxylate, a fumaric ester **3** is formed in which one carbomethoxyl group is *cis* to the bulky elements of **1** and sterically relatively unstable. Protonation of **3** will now form the unconjugated (6.0 μ) ketone salt **5**, which may revert to **3** in base without any geometrical isomerization of the fumarate olefin, but may also slowly isomerize in acid (even its own solution in wet ether) to the crystalline salt **6**. The terminal carbomethoxy is now free to rotate away from the bulky substituted phosphorus and so form the more stable geometrical isomer **7** when neutralized with base. The infrared spectrum of **7** is very similar to that of **3**, while in the n.m.r. spectrum the single proton is shifted downfield to τ 3.96 and is practically unsplit, while the other absorptions are almost identical. In the ultraviolet spectrum both isomers show the absorption of compound **1**[8] plus a longer wave length band, at 367 mμ in **3** and at 403 mμ in **7**; the shorter $\lambda_{\max}$ in the less stable **3** may reflect steric inhibition of resonance in **3** relative to **7**. In acid the longer wave length bands (at 305–318, 367, and 403 mμ)[8] disappear in all three compounds, **1**, **3**, and **7**.

Refluxed in methanolic alkali, both isomers (**3** and **7**) lose triphenylphosphine oxide and afford, besides benzoic acid and acetophenone, a small amount of a colorless material, C$_{13}$H$_{10}$O$_4$, containing all the skeletal carbons of the adduct. The substance is soluble in alkali (but not in bicarbonate), though it exhibits no hydroxyl in the infrared; major carbonyl absorption is found at 5.82 μ. The n.m.r. spectrum shows phenyl absorption as two multiplets at τ 2.2 (2H) and 2.6 (3H), one-proton singlets at τ 2.94 and 3.19, and a singlet (3H) at 6.07. These data are appropriate for an α-pyrone, formulated as **8**; the ultraviolet spectrum is a bimodal curve [$\lambda_{\max}$ 253 mμ (log ε 4.02), 360 (4.06)] similar to those of the natural 6-phenyl-2-pyrones [$\lambda_{\max}$ 233 mμ (log ε 3.99), 332 (4.15)].[9] The enolic γ-lactone isomer would have a lower lactone infrared absorption as well as a lower $\lambda_{\max}$ in the ultraviolet spectrum.[9] Another alkaline degradation product formed concurrently is a decarboxylated ester retaining phosphorus and accorded formula **9** both on the grounds that the terminal carbomethoxyl group is the one saponified in the formation of **8** and that only the terminal carboxyl is readily decarboxylated (as a vinylogous β-keto acid) on mechanistic grounds. Product **9** is similar in spectral and chemical properties to the initial adduct but exhibits only one methyl singlet (τ 6.63) in the n.m.r. spectrum. Taken together these results confirm the structure **3** for the adduct.

An *isomeric adduct* is formed when equimolar amounts of **1** and dimethyl acetylenedicarboxylate are allowed to stand in dry ether. The physical and chemical properties of this new adduct are similar to those of **3** and **7**: the ultraviolet spectrum was more similar to that of **7** (see the Experimental Section) and the infrared spectrum showed the ester (5.80 μ) and conjugated ketone (6.65 μ) bands and a new broad carbonyl band at 6.1 μ; in the HBF$_4$ salt these bands shifts to 5.78, 6.00, and 6.24 μ. In the n.m.r. spectrum the 20 aromatic hydrogens were again a complex multiplet at τ 2–3 and the two ester methoxyls showed 3H singlets at τ 6.27 and 6.84. The remaining single

---

[7] S. T. D. Gough and S. Trippett, *Proc. Chem. Soc.*, 302 (1961).

[8] In all these compounds a group of two or three bands at 263–275 mμ reflects the aromatic absorption of the triphenylphosphorus moiety and this is retained in acid.

[9] A. I. Scott, "Interpretation of the Ultraviolet Spectrum of Natural Products," Pergamon Press Ltd., London, 1964, pp. 79–83, 140–144.

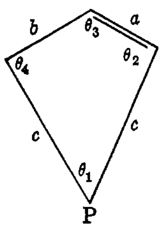
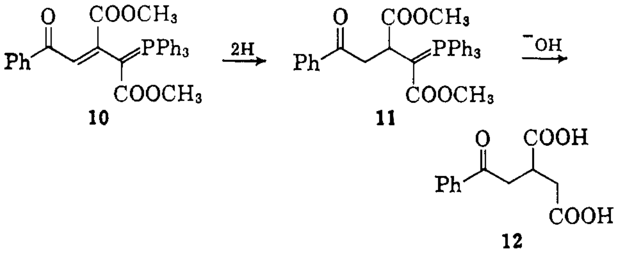


Figure 1.—Angles in an unsaturated phosphorane: a = 1.33 Å.; b = 1.53 Å.; and c = 1.87 Å.

proton appeared as a broad singlet (unresolved doublet?) at τ 4.39. As the major difference from the previous adducts appeared to lie in the 6.1-μ infrared absorption, we tentatively assigned the structure **10** (see Chart II) with the triphenylphosphorylidene group placed adjacent to an ester on the grounds that the ester absorption in $Ph_3PCHCOOCH_3$ is raised to 6.2 μ by the conjugation with phosphorus. Like the other adducts, the new compound yielded benzoic acid, acetophenone, and triphenylphosphine oxide in alkali, although no other products were found, and pyrolysis yielded triphenylphosphine oxide amid charring which prevented isolation of other products. After heating with methanolic acids, the new adduct was recovered unchanged.

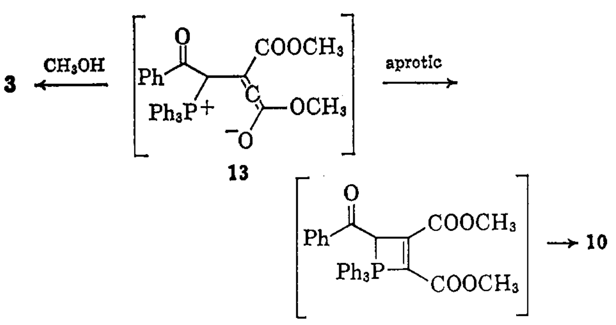
CHART II



The formula **10** was confirmed, however, when it was found that, unlike the previous adducts, the new phosphorane could be reduced by zinc or catalytic hydrogenation to a white crystalline dihydro compound (**11**), the infrared spectrum of which clearly showed the unconjugated ester at 5.78 μ, the phosphorylidene ester at 6.15 μ, and the benzoyl moiety at 5.95 μ. The HBF_4 salt of the dihydro compound also shows the benzoyl group absorption at 5.95 μ but only a single ester band at 5.78 μ, the intense ester absorption at 6.15 μ having disappeared, as it also does on formation of the salts of $Ph_3PCHCOOR$. An ultraviolet spectrum of the dihydro compound recorded against a solution of $Ph_3PCHCOOCH_3$ of the same concentration yielded directly a difference curve showing only a maximum at 238 mμ (log ϵ 4.04), typical of simple benzoyl compounds [*cf.* compound **12** below: λ_{max} 242 mμ (log ϵ 4.05)]; although both these compounds have different spectra in acid, the difference curve in acid is much the same benzoyl absorption, as expected. Treatment of the dihydro compound with alkali led to phenacylsuccinic acid (**12**) which in turn afforded authentic β-phenylethylsuccinic acid on Wolff–Kishner reduction.

The formation of the two adducts provides an interesting confirmation of a recent proposal[5] concerning the mode of additions to acetylenedicarboxylic esters.

CHART III



These additions are envisaged as commencing by attack of a nucleophile in a Michael addition, affording an allenic enolate as the first intermediate (*cf.* **13**, Chart III). In the presence of mobile protons, either in the donor or a protic solvent, this readily collapses to a simple Michael adduct, almost invariably *trans* (*i.e.*, a monosubstituted fumaric acid ester). When no mobile protons are available, the initial intermediate enolate either collapses by internal cyclization or adds to a second mole of acetylenedicarboxylate to form a 1:2 adduct which often can cyclize with more facility (examples in ref. 5). In the present case the first course is that taken in the protic solvent, methanol, yielding the simple *trans* adduct **3**; in the aprotic ether medium, however, the intermediate enolate collapses internally to the four-membered phosphorane **14**, which can then tautomerize to the presumably more stable, conjugated system of the second adduct **10**.

The most common occurrence in aprotic media is addition of the intermediate enolate to a second mole of the acetylene since cyclization to a four-membered ring as in **14** is usually energetically unfavorable. When the ring contains a phosphorus atom, however, as in the present case, this is a much more favored course. Relative to corresponding cyclobutane derivatives, four-membered phosphoranes are less strained since (a) the longer P–C bonds allow bond angles at carbon larger than 90°, and (b) owing to the trigonal bipyramid geometry of the bonding in phosphoranes (five single bonds to phosphorus), the ring can be formed between the apex and perimeter of the trigonal bipyramid at a normal angle of only 90°.

A rough calculation can be made to estimate the energy preference conferred by these circumstances in the following way. The strain energy involved in bond-angle deformation is proportional to the square of the deviation (Δ) of the angle from its normal value. Thus, in the case of **14**, shown in Figure 1, $\Delta_1 = \theta_1 - 90°$; $\Delta_2 = \theta_2 - 120°$; $\Delta_3 = \theta_3 - 120°$; $\Delta_4 = \theta_4 - 109.5°$; and the strain energy $E \propto \Sigma\Delta_n^2$. Variations in one angle provide for the minimization of $\Sigma\Delta_n^2$ and hence for determination of the most favored geometry.[10] Such a minimization in the case at hand (Figure 1) yields $\theta_1 = 71°$, $\theta_2 = \theta_3 = 99°$, and $\theta_4 = 91°$. When the analogous minimization of $\Sigma\Delta_n^2$ for cyclobutene is carried out for comparison (the angles found are $\theta_3 = 94°$, $\theta_4 = 86°$), the resultant angle-

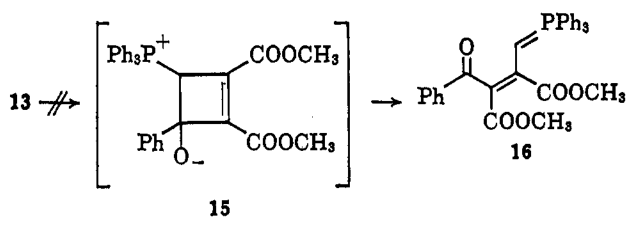
---

[10] In the geometrical calculations, the ring is assumed to be flat; assumption of θ_1 allows the other three angles to be calculated easily. It is also assumed that angle strain is the dominant component in the strain energy of these four-membered rings, and also that the bending-strain constants for the different kinds of bond angles involved are approximately equal.

strain energy is 1.6 times as high as that for the phosphorane.[11]

The conclusion of the argument above that the four-membered phosphorane is substantially preferred over a cyclobutene finds a significant test in the present example, since the enolate **13** can, in principle, collapse not only to phosphorus as in **14** but also to the benzoyl carbonyl, yielding a cyclobutene intermediate **15** which could readily tautomerize to yet another stable isomer **16** (see Chart IV). The evidence above precludes this skeleton for any of the adducts isolated and no evidence of the presence of another similar keto-phosphorane such as **16** was ever found in the mother liquors. The preference of the system **13** for phosphorus cyclization is clear in this choice as well as in the nonformation of any 1:2 adducts by addition to a second mole of acetylenedicarboxylate.

CHART IV



The skeleton of adduct **10** represents in effect a 1,3 shift of phosphorus on the carbon framework. Such 1,3 rearrangements of carbon or hydrogen are exceedingly rare, but the above arguments about the stabilities of the postulated four-center intermediates provide a basis for understanding the difference in the two cases. Several attempts were made to realize direct 1,3 rearrangements in the isomers **3**, **7**, and **10**, for, if an allenic enolate anion (*cf.* **13** from **3** or **7**) can be formed directly from one of these with base, it could lead to a rearranged isomer, *i.e.* **3** or **7** → **10**, or *vice versa.* Boiling **3** in tetrahydrofuran with sodium hydride led to formation of some of isomer **7**, as shown by thin layer chromatography, and similar treatment of **10** led mostly to unchanged **10** and a very small amount of a substance identical with **7** by thin layer chromatography and showing its characteristic 403-mμ ultraviolet absorption. More drastic conditions tended toward decomposition to other products, including triphenylphosphine oxide.

Experimental Section

Melting points are uncorrected; analyses were performed by Miss Heather King of the University of California at Los Angeles and Schwarzkopf Laboratories, Woodside 77, N. Y. Infrared spectra were determined in chloroform or methylene chloride unless otherwise noted on a Perkin-Elmer Infracord, ultraviolet spectra in 95% ethanol on a Cary Model 14, and n.m.r. spectra in deuteriochloroform on Varian HR-60 and A-60 instruments. Spectral data are quoted as follows: principal infrared bands, λ_{max} in μ; ultraviolet absorptions as λ_{max} in mμ (log ε); and n.m.r. peaks at τ values (number of protons as *n*H) and s = singlet, d = doublet, m = multiplet to indicate splitting.

Formation of the Adducts. A.—Triphenylphosphorylideneacetophenone[12] (11.4 g., 30 mmoles) was dissolved in 40 ml. of hot methanol and cooled, whereupon 4.3 g. (30 mmoles) of redistilled dimethyl acetylenedicarboxylate (Matheson Coleman and Bell) was added, and the solution was boiled for 10 min. and allowed to stand overnight. Yellow crystals of **3** (4.6 g., 30%) were filtered and recrystallized from benzene: m.p. 157–168°; infrared 5.83, 6.22, 6.30, 6.62 μ; ultraviolet 225 mμ (log ε 4.55), 267 (3.88), 274 (3.84), 307 (3.75), 367 (3.77); n.m.r. τ 2–3 (20H, m) 4.81 (1H, d, J = 3 c.p.s.), 6.67 (3H, s), 6.97 (3H, s).

Anal. Calcd. for $C_{32}H_{27}PO_5$: C, 73.53; H, 5.22. Found: C, 73.78; H, 4.97.

On briefly heating the methanolic mother liquors with a little H_2SO_4 and working up (see procedure for isomer **7** below), as much as 40% more yield may be obtained as the more stable isomer **7**.

B.—When the same reactants are dissolved in a large volume of anhydrous ether and allowed to stand several days, the solution slowly turned orange and deposited in 50–80% yield yellow crystals of **10**: m.p. 230–231°; infrared 5.80, ~6.1 (br), 6.65 μ; ultraviolet 224 mμ (log ε 4.73), 259 (4.10), 263 (4.11), 405 (4.34); n.m.r. τ 2–3 (20H, m), 4.39 (1H, s–d, unresolved), 6.27 (3H, s), 6.84 (3H, s).

Anal. Calcd. for $C_{32}H_{27}O_5P$: C, 73.53; H, 5.22. Found: C, 73.57; H, 5.39.

Salts of the Adducts.—When a solution of any one of the phosphoranes in methylene chloride was shaken briefly with 25% of (1:1) aqueous fluoroboric acid and the organic layer was dried and evaporated, weight loss to the aqueous layer was negligible but the yellow color disappeared immediately. If the colorless oil so obtained from **3** was redissolved in methylene chloride and shaken with aqueous alkali, the yellow color returned and evaporation of the solvent yielded, practically quantitatively, crystals of **3**, m.p. 165–167°, undepressed on admixture with the initial adduct **3**, and exhibiting an infrared spectrum identical with that of **3** with none of the bands characteristic of **7**. The oily salt showed infrared bands at 5.80, 3.00, 6.28, and 9–10 μ. Dissolved in ether with a drop or two of water added, its solution slowly deposited white crystals (**6**) overnight, which were recrystallized from ether–methylene chloride as colorless blocks: m.p. 175–182°; infrared 5.80, 6.10, 6.20, 6.25, 9–10 μ; ultraviolet 228 mμ (log ε 4.5), 261 (4.02), 268 (4.02), 274 (3.99).

Anal. Calcd. for $C_{32}H_{28}BF_4O_5P$: C, 62.95; H, 4.65. Found: C, 63.01; H, 4.58.

The isomeric adduct **10** on similar treatment yielded colorless crystals: m.p. 160–180°; infrared 5.78, 6.00, 6.24, 9–10 μ. On analogous basification, these afforded the original adduct **10**, identified by mixture melting point and infrared spectrum.

Formation of the Stable Isomer 7.—Solution of the crystalline salt **6** from above in methylene chloride, followed by washing with aqueous alkali, drying, and evaporating, led to orange crystals, m.p. 164–165°, m.m.p. 158–162° with **3**. The infrared spectrum showed bands at 5.82, 6.32, and 6.62 μ and differed from that of **3** in a few different absorptions in the region 7.3–8.7 μ; ultraviolet 228 mμ (log ε 4.53), 266 (3.90), 274 (3.86), 305 (3.74), 403 (3.51); n.m.r. τ 2–3 (20H, m), 3.96 (1H, s, not sharp), 6.71 (3H, s), 6.90 (3H, s). When adduct **3** was dissolved in hot methanol and 1 drop of H_2SO_4 was added, the solution went nearly colorless. After 10 min. of boiling, cooling, shaking with methylene chloride and aqueous alkali, and evaporation of the dried organic layer, the same orange crystals were obtained in near quantitative yield.

Anal. Calcd. for $C_{32}H_{27}O_5P$: C, 73.53; H, 5.22. Found: C, 73.57; H, 5.43.

When the adduct **7** was treated with fluoroboric acid analogously to the treatment of **3** above, evaporation of the methylene chloride yielded the crystalline salt **6** in virtually quantitative yield.

Pyrolysis of the Adducts.—The original adduct **3** (250 mg.) was pyrolyzed in a glass tube at 180° (0.01 mm.) and distilled cleanly (no bulb residue) to two colorless fractions, well separated on the tube. Cutting the tube between them afforded 125 mg (95%) of crystalline triphenylphosphine oxide, recrystallized from methanol to m.p. 151–153° and identified by comparison of infrared spectra and mixture melting point with an authentic sample (m.p. 153°). The other fraction (124 mg.), consisting of oily crystals (**4**), was recrystallized from methanol: m.p.

---

[11] A similar computation for a saturated four-membered phosphorane ring may be made in which $\Delta_1 = \theta_1 - 90°$ and the others are $\Delta_n = \theta_n - 109.5°$. The geometry computed for this circumstance is $\theta_1 = 75°$, $\theta_2 = \theta_4 = 95°$, $\theta_3 = 96°$, while the angle-strain energy for cyclobutane ($\theta = 90°$) is 1.8 times that of the saturated phosphorane. In the fairly common analogous four-centered intermediate involving a P–O bond (as in Trippett's phosphorylidene ketone pyrolysis to an acetylene[7]) the four-membered ring is presumably more favorable yet, since the norm for the C–O–P angle may also be taken as ~90°.

[12] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

83.5–85°; infrared 4.50, 5.80, 6.22 μ; n.m.r. τ 2.7 (5H, m), 3.72 (1H, s), 6.27 (3H, s), 6.32 (3H, s).

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.70; H, 4.97.

Similar pyrolyses on isomer **10** produced a distillate consisting only of crystalline triphenylphosphine oxide, identified as above, and considerable charring in the distilling bulb.

β-Phenylethylsuccinic Acid.—The above product, m.p. 83.5–85° (50 mg.), was hydrogenated in 25 ml. of 95% ethanol containing 33 mg. of platinum oxide. After 80 min. the rate of hydrogenation had slowed considerably; an uptake of 22.5 cc. of hydrogen was recorded (calcd., catalyst = 7 cc.; calcd. for 3 equiv. of H_2 on **4** = 14 cc.) and hydrogenation stopped. Sodium hydroxide (10% solution, 5 ml.) was added and the solution was allowed to stand overnight. The solution was then boiled to remove alcohol, cooled, filtered, and washed with ether, then acidified with concentrated hydrochloric acid and extracted with methylene chloride. Drying and evaporation of the organic layer afforded 37 mg. of oil which crystallized on scratching. Recrystallized from benzene, this yielded colorless needles, m.p. 134–135° (lit.[6] m.p. 136°), of β-phenylethylsuccinic acid: infrared 3–4 (br), 5.82, 5.85 μ; ultraviolet end absorption only. On slow vacuum distillation it yielded an oil with infrared bands at 5.38 and 5.58 μ.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.66; H, 6.36. Found: C, 64.35; H, 5.93.

Saponification of the Adducts. A.—Adduct **3** (1.05 g.) in 15 ml. of methanol was made basic with 7 ml. of 2 *N* aqueous potassium hydroxide and refluxed for 3 hr. Water was added; the solution was washed with ether and acidified with sulfuric acid to a clear pale yellow solution with mild bubbling. After standing 0.5 hr., the solution was again made basic, whereupon it deposited yellow crystals of **9** which on filtration and drying weighed 0.53 g.: m.p. 155–162°, raised to 160–161° on recrystallization from methanol; infrared 5.83, 6.24, 6.67 μ; ultraviolet 267 mμ (log ε 3.54), 274 (3.54), 305 (3.43). Like adduct **3**, the yellow color of a methylene chloride solution was destroyed on shaking with aqueous fluoroboric acid; the oily fluoroborate salt showed the typical BF_4^- infrared absorption at 9–10 μ as well as bands at 5.80 and 5.96 μ but could not be induced to crystallize. Pyrolysis of **9** (85 mg.) yielded a crystalline mixture (31 mg.) of triphenylphosphine and its oxide, m.p. 78–80°, identified by infrared spectra.

Anal. Calcd. for $C_{30}H_{23}O_3P$: C, 77.57; H, 5.42. Found: C, 77.46; H, 5.64.

When the yellow aqueous basic filtrate remaining above was washed with methylene chloride and then acidified below pH 4, it deposited an oily precipitate, which was extracted with methylene chloride. Drying and evaporating the organic layer yielded 0.31 g. of an oil which crystallized on standing and could be recrystallized from methanol to very pale yellow needles of **8**: m.p. 123–124°; infrared 5.82, 6.10, 6.41 μ; ultraviolet 253 mμ (log ε 4.02), 360 (4.06); n.m.r. τ 2.23 (2H, m), 2.57 (3H, m), 2.94 (1H, s), 3.19 (1H, s), 6.07 (3H, s).

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.86, 67.93, 68.04; H, 4.44, 4.62, 4.48.

Hydrogenation of **8** in neutral or alkaline solution always absorbed more than 2 equiv. of hydrogen fairly rapidly and gave mixtures of products not easily separated. Product **8** was also obtained by analogous alkaline treatment of isomer **7**.

B.—Each of the adducts **3**, **7**, and **10** was separately refluxed for several days in a methanolic solution conatining 5% sodium hydroxide. Steam distillation of the resulting solution provided acetophenone as an oil identified as its 2,4-dinitriphenylhydrazone by mixture melting point with an authentic sample. Extraction of the basic solutions next yielded triphenylphosphine oxide in near quantitative yields. Acidification and extraction of the residual aqueous solutions afforded pure samples of benzoic acid, m.p. 122°, on sublimation.

Bromination of the Isomers.—Adduct **3** (1.0 g., 2 mmoles) in methylene chloride was shaken with 10 ml. of saturated bromine water (2 mmoles). Removal of the organic phase affords yellow crystals of the monobromo derivative, which were crystallized from methanol (1.0 g., 87%): m.p. 158–159°; the infrared and ultraviolet spectra differed from the original adduct **3** only in minor detail; n.m.r. τ 2.7 (20H, m), 6.54 (3H, s), 6.96 (3H, s).

Anal. Calcd. for $C_{32}H_{26}BrO_5P$: C, 63.90; H, 4.36; Br, 13.29. Found: C, 64.05; H, 4.53; Br, 12.90.

Isomer **7** was brominated similarly to give a very similar compound in all respects, m.p. 153–155°, m.m.p. 152–155°. Adduct **10** also yielded in the same way a bromo derivative, m.p. 209–210°, with spectral characteristics closely resembling those of adduct **10** itself.

Hydrogenation of the Isomer.—Highly purified samples of adducts **3** and **7** were hydrogenated both in methanol and glacial acetic acid with as much as equal weights of platinum oxide with only negligible uptake of hydrogen; the same was true when sulfuric acid was added to form the salts. However, 3.10 g. of adduct **10** and 107 mg. of platinum oxide, on hydrogenation in 50 ml. of glacial acetic acid, absorbed 191 cc. of hydrogen (1.2 equiv.) in 6 hr. The filtered solution was evaporated to a small volume three times with added carbon tetrachloride and excess aqueous bicarbonate added. The reddish residue was extracted with methylene chloride, dried, and evaporated and the resultant semisolid was crystallized from methanol, yielding 2.50 g. (80%) of off-white crystals, recrystallized to colorless needles of dihydro compound **11**, m.p. 192–193°, from methanol: infrared 5.78, 5.95, 6.15 μ; n.m.r. τ 2.2–2.8 (20H, m), 6.44 (6H, s), 7.05 (3H, m); ultraviolet 228 mμ (4.53); the ultraviolet spectrum of **11** *vs.* an equal concentration of $Ph_3PCHCOOCH_3$ showed λ_{max} 238 mμ (log ε 4.04) neutral, and 239 mμ (log ε 4.05) with 2 drops of HCl in each cell.

Anal. Calcd. for $C_{32}H_{29}O_5P$: C, 73.27; H, 5.58. Found: C, 73.22; H, 5.58.

The same dihydro compound **11** was formed by treatment of adduct **10** in refluxing methanol containing several equivalents of sulfuric acid with zinc dust over a period of 1 hr. Treatment of **11** with fluoroboric acid as in the above cases yielded a colorless oil (infrared 5.78, 5.95, 9–10 μ) which regenerated **11** when made basic. Long reflux of **11** in benzaldehyde, attempting a Wittig reaction, led only to the isolation of starting material. Several brominations of **11** led to mixtures containing no evidence of adducts **3**, **7**, or **10** on thin layer chromatography.

Reaction of Dihydro Compound 11 with Alkali.—Dihydro compound **11** (538 mg.) was dissolved in 15 ml. of methanol, 2 ml. of 6 *M* aqueous potassium hydroxide was added, and the solution was refluxed 2.5 days. The methanol was evaporated after acidification with 6 *M* hydrochloric acid and methylene chloride and aqueous bicarbonate were added. The organic layer, on evaporation, yielded a neutral fraction of 300 mg., with an infrared spectrum essentially that of triphenylphosphine oxide. Crystallization from benzene–petroleum ether (b.p. 00–00°) after charcoaling yielded 124 mg., m.p. 151–153°, identical with an authentic sample. The acid fraction, obtained by continuous chloroform extraction of the acidified aqueous layer, afforded 154 mg. (62%) of crude crystalline substance, recrystallized from methanol–chloroform to 93 mg. (40%) of phenacylsuccinic acid: m.p. 159–160°[13]; infrared 3.3–3.5, 5.88 μ (both broad peaks); ultraviolet 242 mμ (log ε 4.05).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12, equiv. wt., 118. Found: C, 60.87; H, 5.14, equiv. wt., 120.

Reduction of Phenacylsuccinic Acid (12).—Phenacylsuccinic acid (**12**, 118 mg.) was mixed in 1.4 ml. of ethylene glycol with 210 mg. of solid potassium hydroxide and 4 drops of 85% hydrazine hydrate and heated to reflux for 1.5 hr. Some water was allowed to evaporate and the temperature rose to 235°. The temperature was adjusted to 200–210° and heating was continued for 4 hr. The brown residue was washed into a continuous extractor with 7 ml. of water and extracted with chloroform for 9 hr., then acidified, and extracted with fresh chloroform for 4 hr. more. The light brown product was charcoaled and twice crystallized from benzene, affording 35 mg. of colorless crystals, m.p. 133.5–135°, m.m.p. 134–135°, and infrared spectrum identical with that of the previous sample of β-phenylethylsuccinic acid.

---

[13] H. R. Ing and W. H. Perkin, Jr. [*J. Chem. Soc.*, **125**, 1814 (1924)] reported its preparation in unspecified yield, m.p. 165°; we were not able to reproduce their experiment.