TABLE I

NMR DATA OF MALEALDEHYDIC AND FUMARALDEHYDIC ACIDS

	Ch	emical shifts	s, δ	-Couplin	g constar	ıts, Hz—
Compd	$\mathbf{H}_{\mathbf{A}}$	$H_B$	$\mathbf{H}_{\mathbf{X}}$	$J_{ m AB}$	$J_{\mathrm{AX}}$	$J_{\rm BX}$
$1b^a$	6.25	6.20	7.41	1.2	1.2	5.7
2 <sup>b</sup>	6.91	6.72	9.77	15.8	0.4	7.8
ª In ac	etone- $d_6$ .	<sup>b</sup> In DMSC	)-d <sub>6</sub> .			

spectively.<sup>7</sup> We found that 2 can be prepared conveniently in 26% yield by treating a crude photooxygenation mixture containing **1b** and **1c** with sodium bicarbonate. No **2** was detected in the mixture by tlc before the bicarbonate was added. Likewise, treating pure **1b** with bicarbonate for 2 days gave an isomerization mixture containing **2** and **1b** in the ratio of approximately 3:2. The three C protons of **2** exhibit an ABX pattern with coupling constants near those reported for *trans*-crotonaldehyde.<sup>10</sup> The typically large transvinyl proton coupling constant of 15.8 Hz in **2** is also near that found for *trans-β*-acetylacrylic acid.<sup>9</sup>

Since an initial attempt to hydrolyze 1a with 0.1 N HCl at room temperature resulted in less than 50% hydrolysis, the compound was hydrolyzed with refluxing 2 N HCl by the method of White.<sup>5</sup> Purification of the ethyl acetate extractables by adsorption chromatography gave, as the major product, 28% of crystalline 1b, plus less than 2% of 2. Identity of the hydrolysis products from 1a was established by ir, tlc, and melting point.

Alkaline hydrolysis of 1a was carried out at room temperature with 0.1 N NaOH according to the procedure of Burkhardt, *et al.*<sup>6</sup> In view of the ease of bicarbonate-induced ring opening and concomitant isomerization of 1b to 2, the expected product in this reaction was again 2. Indeed, examination of the ether extract from the acidified reaction mixture by ir and tle showed 2 as the major product, plus a minor amount of 1b. Thus, contrary to implications of earlier reports,<sup>5,6</sup> formation of 2 from 1a is favored under alkaline conditions. Silica gel chromatography of the ether extractables afforded a 24% yield of 2, plus less than 1.5% 1b. The low yield of 2 is not due to loss of significant amounts of material on the silica, but rather to formation of considerable polymeric material during hydrolysis.

#### Experimental Section

Melting points were determined on a Fisher-Johns block and are uncorrected. The following spectrometers were used: ir, Perkin-Elmer 337 (CHCl<sub>3</sub>); uv, Beckman DK-2A (EtOH); nmr, Varian HA-100 with TMS as an internal standard.<sup>11</sup> Thin layer chromatograms were run on silica gel G coated plates.

Malealdehydic Acid (1b).—Oxygen was passed into an irradiated mixture of 100 g of furfural and 2.0 g of eosin (yellowish) in 1400 ml of  $H_2O$ -EtOH (1:1) for 4 days. Light was provided by a circular arrangement of 26 20-W cool-white fluorescent lamps; wavelengths shorter than 460 nm were filtered out by an aqueous solution of 1.25 M CaCl<sub>2</sub>.<sup>12</sup> After most of the solvent was removed, the solution was diluted with  $H_2O$  and filtered to remove eosin. The filtrate was washed with CCl<sub>4</sub> and extracted thoroughly with ethyl acetate. After the ethyl acetate extract was dried (Na<sub>2</sub>SO<sub>4</sub>), the solvent was removed; the residual oil crystallized upon refrigeration. The crystals were washed with benzene and recrystallized from CHCl<sub>3</sub>-benzene to give 25.8 g (25%) of 1b: mp 53-56°; additional recrystallizations raised the melting point to 54.5-56.5° (lit.<sup>7</sup> mp 58-59°); tle  $R_f$  0.44 [CHCl<sub>3</sub>-acetone-acetic acid (85:10:5), sprayed with 3% ceric sulfate in 3 N H<sub>2</sub>SO<sub>4</sub>, and heated at 120°]; ir 3580 (OH), 1790, 1760 (C==O), 1115, 1003 cm<sup>-1</sup>; uv max 202 nm ( $\epsilon$  6870); phenylhydrazone<sup>8</sup> mp 159-161°, tle  $R_f$  0.48 [hexane-ether-acetic acid (47:50:2), I<sub>2</sub> vapor].

Fumaraldehydic Acid (2).—The reaction was carried out as described for 1b. Two-thirds of the solvent was removed, 126 g of NaHCO<sub>3</sub> was added, and the mixture was kept at room temperature for 3 days. The solution was acidified to pH 1.5 with 10 N HCl, washed with CCl<sub>4</sub>, and extracted thoroughly with ethyl acetate. The crystalline residue, obtained by drying (Na<sub>3</sub>SO<sub>4</sub>) and removal of the ethyl acetate solvent, was passed through 600 g of silica gel (70–325 mesh). Elution of the column with acetone–CHCl<sub>3</sub> (1:4), concentration of the fractions containing 2, and recrystallization from acetone–CHCl<sub>5</sub> gave 26.8 g (26%) of 2: mp 125–126°; additional recrystallizations raised the melting point to 126.5–127° (lit.7 mp 127°); tle  $R_t$  0.55 [CHCl<sub>3</sub>– acetone–acetic acid (85:10:5), sprayed with 3% ceric sulfate in 3 N H<sub>2</sub>SO<sub>4</sub>, and heated at 120°]; ir 3510 (OH), 1740, 1700 (C==O), 1100, 978 cm<sup>-1</sup>; uv max 216 nm ( $\epsilon$  11,000); phenylhydrazone<sup>4</sup> mp 159.5–161°, mixture melting point with 1b phenylhydrazone 146–151°, tlc  $R_t$  0.33 (hexane–ether–acetic acid, 47:50:2).

Isomerization of Malealdehydic Acid (1b).—A solution of 1.0 g of 1b and 2.1 g of NaHCO<sub>3</sub> in 20 ml of H<sub>2</sub>O was kept at 20° for 2 days. The solution was acidified to pH 1 with 4 N HCl and extracted with ethyl acetate. The extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated, leaving 780 mg of residue. Examination of the ir carbonyl region of the residue showed compound 2 and starting 1b in approximately a 3:2 ratio.

Acid Hydrolysis of 4-Acetamido-4-hydroxy-2-butenoic Acid  $\gamma$ -Lactone (1a).—A solution of 1.0 g of 1a (obtained by synthesis<sup>8</sup>) in 40 ml of 2 N HCl was refluxed for 3 hr, cooled, and extracted with ethyl acetate. The ethyl acetate extract was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed. Chromatography of the residue on 25 g of silica gel (CHCl<sub>3</sub> eluent) plus crystallization from CHCl<sub>3</sub>-benzene gave 202 mg (28%) of 1b, mp 53.5-56.5°. Ir analysis of the carbonyl region of the mother liquor indicated less than 10 mg (2%) of 2.

Alkaline Hydrolysis of 4-Acetamido-4-hydroxy-2-butenoic Acid  $\gamma$ -Lactone (1a).—A solution of 1.0 g of 1a in 78 ml of 0.1 N NaOH was kept at room temperature for 16 hr. The solution was acidified to pH 1.5 with 1 N HCl and extracted with ether. After the ether extract was dried (Na<sub>2</sub>SO<sub>4</sub>), the solvent was removed. The residue (410 mg) was examined by ir and tlc and chromatographed on 25 g of silica gel [acetone–CHCl<sub>3</sub> (5:95) eluent]. Recrystallization from CHCl<sub>3</sub> gave 169 mg (24%) of 2, mp 126.5–127.5°. Subsequent column fractions were combined and by ir analysis contained less than 9 mg (1.5%) of 1b.

**Registry No.**—1a, 16275-44-8; 1b, 14032-66-7; 2, 4437-06-3; furfural, 98-01-1.

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# "Dimers" from the Reaction of Propargyl Halides with Organometallic Reagents

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In connection with another study, we had occasion to prepare di-*tert*-butylacetylene (1). Its synthesis was first described by Hennion and Banigan,<sup>1</sup> then

(1) G. F. Hennion and T. F. Banigan, Jr., J. Amer. Chem. Soc., 68, 1202 (1946).

<sup>(10)</sup> A. W. Douglas and J. H. Goldstein, J. Mol. Spectrosc., 16, 1 (1965).
(11) Mention of firm names or trade products is for identification only and does not imply endorsement by the U. S. Department of Agriculture.

<sup>(12)</sup> C. R. Masson, V. Boekelheide, and W. A. Noyes, Jr., in "Technique of Organic Chemistry," Vol. 2, 2nd ed, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, p 283.

later by Puterbaugh and Newman,<sup>2</sup> who used the unexceptional reactions below. Each step proceeded in



reasonable yield, but the purification of 1 was laborious because several chemically similar side products accompanied its formation. Among these was a material (A) variously described as a high-boiling unsaturate<sup>1</sup> and a crystalline "dimer,"<sup>2</sup> the structure of which was tentatively assigned as 2,2,5,5,6,6,9,9octamethyldeca-3,7-diyne (4) on the basis of elemental



analysis, (osmotic?) molecular weight, and hydrogenation.

Somewhat later Jacobs and Prempree<sup>3</sup> carried out an extensive study of the coupling reactions of propargyl chlorides with organometallic reagents. They found that the reaction of **3** with methyllithium in ether gave a low (isolated) yield of **1** accompanied by its allenic isomer 2,2,3,5-tetramethyl-3,4-hexadiene (**5**) in the

$$3 + CH_3Li \rightarrow 1 + C = C = C + B$$

ratio 65:35, respectively. The major isolated product, however, was a solid (B) of mp  $100-102^{\circ}$  (that of A was  $112.5-113^{\circ}$ ), which was also assigned structure 4 on the basis of elemental analysis and <sup>1</sup>H nmr.

Thus there remained some uncertainty regarding the identity and properties of A (= B = 4?), as well as a lack of knowledge about the mechanism of its formation.

The exact mechanisms of reactions involving methyllithium are known to be quite complex,<sup>4</sup> because this reagent is oligomeric in solution. Nonetheless, one can write two mechanistic extremes for the formation of **4** under these conditions. The first involves preliminary halogen-metal exchange<sup>5</sup> and subsequent

(2) W. H. Puterbaugh and M. S. Newman, J. Amer. Chem. Soc., 81, 1611 (1959).

(3) T. L. Jacobs and P. Prempree, *ibid.*, **89**, 6177 (1967).

(4) For continuing timely reviews on organolithium chemistry, see W. H. Glaze, Organometal. Chem. Rev., 4, 161 (1968); 5, 189 (1969); 6, 1 (1970).
(5) The mechanism of Wurtz-type reactions between alkyllithiums and alkyl iodides and bromides can involve caged radicals [see, for example, H. R. Ward, R. G. Lawler, and R. A. Cooper, J. Amer. Chem. Soc., 91, 746 (1969)]. There is evidence, however, that halogen-metal exchange and subsequent coupling reactions of conjugated systems may prefer an "ionic" mechanism [J. Sauer and W. Braig, Tetrahedron Lett., 4275 (1969); W. D. Korte, L. Kinner, and W. C. Kaska, *ibid.*, 603 (1970); L. H. Sommer and W. D. Korte, J. Org. Chem., 35, 22 (1970)]. The two mechanistic extremes above are classified on the basis of the step leading to 4: is the precursor radical-like?



attack by a tertiary carbanion on a tertiary halide (!) while the other involves electron transfer followed by dimerization of the incipient radical.

With either of the above two mechanisms there is the possibility (even the likelihood in the case of a mechanism involving propargyl radicals<sup>6</sup>) that at least one allenic system might be incorporated into A (= B?). Although the <sup>1</sup>H chemical shifts might distinguish between 4 and 6, with so much proximate unsaturation



an assignment based solely on this could be incorrect. In the hope of unifying the earlier work<sup>1-3</sup> and unequivocally establishing the structure of A (= B = 4?), we reinvestigated the reaction of 3 with methyllithium in ether.

When 3 was treated with a slight excess of methyllithium at 25°, three major and at least three minor products (the latter totaling *ca*. 1%) were observed by glc (Table I). The two most volatile major products

TABLE I

PRODUCTS FROM THE REACTION OF 3 WITH METHYLLITHIUM<sup>a</sup> -Mol %  $4^d$ 5 Conditions Temp. °C 1 2560.0 24.715.33 added to CH<sub>3</sub>Li 25.225 59 4 15.4CH<sub>3</sub>Li added to 3

<sup>a</sup> Although these values are relatively percentages within the product mixture, the product masses indicate that yields are virtually quantitative. See Experimental Section. <sup>b</sup> Reaction times 24.7 and 24.3 hr, respectively. <sup>c</sup> Determined by discintegrated peak areas which were corrected for differences in detector response factors. Precision is estimated to be  $\pm 0.2\%$ , with accuracy similar. Each of the products was stable to the reaction conditions. <sup>d</sup> Recall that each mole of **4** requires 2 mol of **3**.

were separated from the third by distillation, and from one another by preparative glc. They were shown to be the expected products 1 and 5. The least volatile major product was isolated by sublimation and recrystallization.<sup>7</sup> This compound had mp  $112.4-112.7^{\circ}$  and

(6) P. S. Engel and D. J. Bishop, J. Amer. Chem. Soc., 94, 2148 [1972).

(7) Compound 4 is exceptionally volatile for a solid. It sublimes at  $90^{\circ}$  (1 atm), and care must be exercised to avoid volatilization during recrystallization from hot solvents and melting-point determinations. was >99% pure by glc. Its mass spectrum (Table II) confirmed the molecular formula  $C_{18}H_{30}$ , as well as ex-

	TABLE II	
	70-eV Mass Spect	RUM OF 4
m/e	Rel intensity	Assignment
246	5	$M \cdot +$
231	15	$M - CH_3$
189	10	$M - C_4 H_9$
165	8	
149	26	
123	100ª	$M/2^{+}$ (or $M^{+2}$ )
109	32	
107	26	
95	20	
93	17	
91	30	
81	84	
69	34	
67	41	
57	42	$C_4H_9^+$
55	32	
41	44	
1.		

<sup>a</sup> Base peak.

hibiting a base peak at m/e 123 for the symmetrical fragmentation expected of 4. The ultraviolet spectrum (pentane) showed only end absorption ( $\epsilon_{210 \text{ nm}}$  150), suggesting that the compound did not possess conjugated unsaturation (such as in 6). Its <sup>1</sup>H nmr spectrum consisted of singlets at  $\delta$  1.19 and 1.21 (those for B occur at  $\delta$  1.17 and 1.20<sup>3</sup>) and, although the exact integration was difficult owing to the proximity of the peaks, the ratio was close to 3:2, respectively. We recently established the normal position for methyl groups  $\beta$  to a carbon-carbon triple bond ( $\delta$  1.23  $\pm$ 0.03)<sup>8</sup> and the above values fall squarely in this region.

It would seem that the (as yet unreported) infrared spectrum of 4 would provide confirmation of its structure, by ruling out 6 and 7. Unfortunately, at normal concentrations (10% in carbon tetrachloride) and path lengths (0.05 mm) no absorptions could be detected for triple bonds or allenic systems. However, examination of a saturated solution through a path of 0.2 mm revealed two extremely weak bands<sup>9</sup> ( $\epsilon \sim 1$ ) at 2225  $\pm 3$  and  $2278 \pm 3 \text{ cm}^{-1}$ , while the 1900-2000-cm<sup>-1</sup> region remained totally flat. Because these two values were nearly equally displaced above and below the band positions for 2 and 3 (2260  $\pm$  5 cm<sup>-1</sup>), perhaps the stretching of the two symmetry-equivalent triple bonds in 4 might be coupled through a combination interaction. Unfortunately, there were bands at  $1109 \pm 1$  (m) and 1141  $\pm$  1 cm<sup>-1</sup> (s) whose first overtones would be exceedingly close to the above values. The Raman spectrum of 4 proved that the former explanation was indeed correct, by exhibiting bands at 2222 and 2274  $cm^{-1}$  (intensity ratio 9:1, respectively). Again no absorptions were observed in the region 1900-2000  $cm^{-1}$ . The structure of A (= B = 4) is thus unambiguously confirmed, and the symmetry of the system allows significant vibrational coupling between the triple bonds.

(8) R. S. Macomber, J. Org. Chem., 37, 1205 (1972).

(9) It is well known that triple bond stretching absorptions for relatively symmetrically substituted acetylenes are often weak or absent owing to the operation of the dipole moment selection rule in infrared spectroscopy. This limitation is of course lifted in Raman spectroscopy. With the structure of 4 secure, what could be said about the mechanism of its formation? As can be seen from Table I, the mode of addition has essentially no effect. If the reactants are mixed immediately, the reaction  $(25^{\circ})$  proceeds 20% after 1.0 hr and 35% after 1.5 hr (as gauged by monitoring the disappearance of 3 by glc). Yet, even if addition of reactants takes place slowly (1.0 hr), the relative amounts of products are nearly identical.

It was possible that, if the reaction involved dimerization of caged radicals, it might exhibit chemically induced dynamic nuclear polarization (CIDNP)<sup>10</sup> when carried out in an nmr cavity. A solution of **3** in ether was added to a solution of methyllithium in the probe at 35°, and the spectrum was repeatedly scanned. No evidence for enhanced emission or absorption could be detected in the lines of any product throughout the reaction.<sup>11</sup>

It is clear from the lack of addition effects that, regardless of the detailed mechanism, the outcome of each encounter of a methyllithium "molecule" with a molecule of 3 is determined at the instant of that encounter. This is certainly consistent with an all-ionic mechanism such as 1 above. It would be true for mechanism 2 only if the ratio of radical escape (and dimerization to 4) to collapse (to 1) were independent of concentration effects. The absence of CIDNP, while suggestive of nonradical pathways forming 1 and 5, is meaningful for 4 only if the mechanism leading to 4 is dependent on and similar to those leading to 1 and 5. Finally, we were unable to detect ethane or other products which might have arisen from the methyl radicals required in mechanism 2. For these admittedly inconclusive reasons, we prefer mechanism 1 at this point.

It is significant that, even under such basic conditions as these, **3** is stable toward dehydrochlorination to **8**, even though similar propargyl halides yield enynes under comparable conditions.<sup>3</sup> An authentic sample of **8** was produced by the pyridine-promoted elimination of HCl from **3**, and it was found to be well resolved from **1** and **5** by glc.<sup>12</sup>



Finally, the structure of **4** is interesting in another regard. Of all the compounds one might design to cyclize to cyclobutadienes,<sup>13</sup> **4** should be an excellent candidate, owing to the twin *gem*-dimethyl groups,

(10) For a recent review on the phenomenon of CIDNP, see H. R. Ward, Accounts Chem. Res., 5, 18 (1972).

(11) Although this observation is suggestive of nonradical processes leading to 1 and 5, it is of questionable value in the case of 4. Because 4 is presumed to arise from a symmetrical dimerization ( $\Delta g = 0$ ), net polarization is normally not expected.<sup>10</sup> and only multiplet effects would be anticipated. Since the pmr spectrum of 4 consists solely of singlets, lack of CIDNP in its spectrum does not rule out a radical mechanism for its formation. It should also be noted that the ether proton signals partially observed.

(12) Interestingly, gle analysis of **3** showed significant amounts of **8** (up to 15%) unless the injection port was kept at ambient temperature.

(13) See, for example, W. D. Huntsman and H. J. Wristers, J. Amer. Chem. Soc., 89, 342 (1967); D. E. Applequist, et al., ibid., 94, 4272 (1972). which help favor conformations from which cyclization is accessible.<sup>14</sup>



Several experiments were carried out to determine if this was the case. A sample of 4 could be heated to  $170^{\circ}$  (neat, sealed tube) for 23.5 hr without change. Next, the compound was irradiated at 253.7 nm under a variety of conditions, which included direct irradiation in degassed pentane (see uv spectrum above) and photosensitization by solvent (degassed acetone and benzene). In each case, after irradiation for *ca*. 23 hr, 4 was found to be totally stable; only products arising from primary photoprocesses of the solvents were observed.

A more promising method for stimulating intramolecular cycloadditions of triple bonds has recently been described by King,<sup>15</sup> involving the reaction of  $\pi$ -cyclopentadienylcobalt dicarbonyl (9) with cyclic diynes.



Indeed the reaction of 4 with 9 provided in low yield a deep red-orange, air-stable compound (C), but its mass spectrum and elemental analysis disappointingly indicated a molecular formula of  $C_{24}H_{35}OCo$ , with one retained carbon monoxide. A possible assignment was a structure with only one of the triple bonds co-ordinated to the cobalt, as in 11. However, the spec-



tral data for C (Experimental Section) immediately ruled this out. Although the pmr spectrum indeed showed two types of methyl groups (one strongly de-

(14) For a recent invocation of the gem-dimethyl effect, see M. Harfenist and E. Thom, J. Org. Chem., **37**, 841 (1972). shielded at  $\delta$  1.54 and one mildly deshielded at 1.27), it showed but one 18-proton singlet for the *tert*-butyl protons. Moreover, the ir spectrum exhibited no bands in the region 2850–1600 cm<sup>-1</sup>, but a very intense band at 1595 cm<sup>-1</sup>, ruling out metal carbonyls and triple bonds! A structure which fulfills all the data arises from cycloaddition of the triple bonds in 1 with a molecule of carbon monoxide to give a  $\pi$ -cyclopentadienonecobalt complex (12), in much the same way that di-



phenylacetylene reacts with  $9^{16}$  to yield  $\pi$ -cyclopentadienyltetraphenylcyclopentadienonecobalt (ir 1590 cm<sup>-1</sup>).

Thus, although the gem-dimethyl effect should facilitate the cycloaddition as well as stabilizing the product, the ring strain, steric hindrance of the *tert*-butyl groups, and antiaromaticity associated with the incipient bicyclic cyclobutadiene 10 are apparently more significant, and cause a detour to the cyclopentadienone. Nonetheless, this reaction provides even more evidence for the structure of 1.

### **Experimental Section**

General.—The microanalysis was performed by Chemalytics, Tempe, Ariz. The following instruments were employed: pmr (carbon tetrachloride solution, internal TMS), Varian A-60; mass spectra, Hitachi RMU-7; uv, Cary Model 14; ir, Perkin-Elmer 337. Melting points were determined with sealed capillaries in an oil bath, and *are* corrected. Analytical glc was carried out with a Hewlett-Packard Model 700 (TC detection) equipped with two 10 ft  $\times$  0.125 in. aluminum columns packed with 12% squalane on 80/100 Chromosorb W-AW DMSC. Using the separation parameters below, the retention times for all relevant compounds were observed to be as compiled in Table III: injection port<sup>12</sup> 60°; helium flow rate 30 cc/min; column temperature 65° for 2 min, then programmed to 130° at 30°/min.

	TABLE III	
	GLC RETENTION TIMES	
Compd	Retention time, min	Response factor <sup>a</sup>
1	1.10	1.00
2	2.60	
3	3.35	
4	7.5	0.795
5	2.40	1.11
8	1.60	
Decane	4.9	

<sup>a</sup> Defined by the equation moles = factor  $\times$  area, with a value of 1.00 arbitrarily assigned to 1.

Preparative glc was performed on a Varian Model 700 preparative gas chromatograph, fitted with a 5 ft  $\times$  0.25 in. steel column packed with 3% SE-30 on 100/120 Diatomite CLO. The separation parameters were injection port 128°, column temperature 79°, helium flow rate 46 cc/min. Under these conditions the retention times of 1 and 5 were 1.6 and 2.7 min, respectively.

2,5,5-Trimethyl-3-hexyn-2-ol (2) was prepared essentially as previously described,<sup>1,2</sup> except that *tert*-butylethynyllithium

(16) M. D. Rausch and R. A. Genneti, J. Org. Chem., 35, 3888 (1970).

<sup>(15)</sup> R. B. King and A. Efratz, J. Amer. Chem. Soc., 94, 3021 (1972).

(from the acetylene and methyllithium) was substituted for the Grignard reagent. This method gives yields of 70%, about 15% lower than the other method: <sup>1</sup>H nmr  $\delta$  1.20 (s, 9 H), 1.44 (s, 6 H), 2.12 (s, 1 H); ir 3400 (broad), 2255 cm<sup>-1</sup>.

**2-Chloro-2,5,5-trimethyl-3-hexyne (3)** was prepared as before<sup>1,2</sup> by passing HCl gas through a pentane solution of 2 at  $-15^{\circ}$  for 6 hr. The yield was 85%:<sup>12</sup> <sup>1</sup>H nmr  $\delta$  1.21 (s, 9 H), 1.78 (s, 6 H); ir 2260 cm<sup>-1</sup>.

Reaction of 3 with Methyllithium (Supplied by PCR). A. Addition of 3 to Methyllithium.—To 15.4 ml (37 mmol) of freshly opened 2.4 M methyllithium in ether at room temperature under nitrogen was added a solution of 4.00 g (25.2 mmol) of 3 in 5.0 ml of ether over 60 min. The mixture was stirred magnetically throughout the reaction. The solution became cloudy (suspended lithium chloride) about 30 min after addition ceased. After 24.7 hr 20 ml of water-saturated ether was added to the milky suspension, followed by 7 ml of ether-saturated water, and 2 ml of 1 N sulfuric acid to partially neutralize the solution. The ether phase was separated and immediately analyzed by glc. The aqueous phase was neutralized and extracted with  $3 \times 10$ ml of ether. The combined ether solutions were washed once with saturated aqueous sodium chloride and dried at room temperature over molecular sieves. Product isolation is described below.

**B.** Addition of Methyllithium to 3.—To a solution of 1.77 g (11.2 mmol) of 3 in 2.0 ml of ether at room temperature under nitrogen was added 6.26 ml (15 mmol) of 2.6 M methyllithium in ether over 60 min. Cloudiness became apparent immediately. After 24.3 hr the mixture was worked up as above and analyzed.

**C.** Product Isolation.—The ether solutions from A and B, containing the total products from 36.4 mmol of **3**, were combined and found to exhibit the mole ratio of 1:5:4 of 59.8:24.9:15.3. Since 1 mol of **4** derives from 2 mol of **3**, the above mixture should contain (assuming quantitative yield) 2.61 g of 1, 1.09 g of **5**, and 1.18 g of **4**, totaling 4.88 g. The solution was slowly distilled at 1 atm through a 9-in. Vigreux column until nearly all of the ether had been collected (bp  $34^{\circ}$ ). This ether contained  $<10^{-2}$  mol % 1. The pot residue (4.90 g), containing 5% ether by glc, was flash distilled down to 0.2 mm into a Dry Ice-acetone cooled receiver. The distillate (2.62 g) was redistilled to yield 2.24 g (45%) of ether, 1, and 5 in the mole ratio 5:69.7:24.1. The boiling point of this mixture was  $56-77^{\circ}$  (152 mm); earlier fractions were richer in 1, later fractions in 5. When run on the mole scale, distillation alone will separate 1 from  $5,^{1,2}$  while at this level preparative glc is preferable.

this level preparative glc is preferable. **Di**-tert-**butylacetylene**  $(1)^{1-3}$  had <sup>1</sup>H nmr  $\delta$  1.17; ir no C=C discernible.<sup>9</sup>

**2,2,3,5-Tetramethyl-3,4-hexadiene** (5)<sup>3</sup> had <sup>1</sup>H nmr  $\delta$  1.01 (s, 9 H), 1.62 (s, 3 H), 1.65 (s, 6 H); ir 1960 cm<sup>-1</sup>.

Isolation of 4.—The combined semisolid residues from the flash and subsequent distillations were combined (2.6 g) and sublimed at 0.15 mm bulb-to-bulb to give 1.10 g (12%) of crude 4. The sole contaminant was 5% of a minor product with slightly greater retention time.<sup>17</sup> Acetonitrile recrystallizations gave a high recovery of material with mp 109–110°, still contaminated with 3% of the minor product. Three recrystallizations of the crude material from ethanol gave >99% pure 4, mp 112.4–112.7°, but the recovery was only 20–30%. The spectral data for 4 are given in the text.

**Reaction of 3 with Pyridine.**—To an nmr tube containing 40 mg of **3** and 2 drops of TMS was added 0.4 ml of dry pyridine. The tube was sealed and heated to 88° for 44 hr. Upon cooling the solution deposited crystals of pyridine hydrochloride. The tube was centrifuged and the spectrum of its contents was recorded, showing 100% conversion to 8: <sup>1</sup>H nmr  $\delta$  1.24 (s, 9 H), 1.87 (d of d, J = 1.5, 0.9 Hz, 3 H), 5.20 (sym m, 1 H). No attempt was made to isolate 8, owing to the known proclivity of enynes toward polymerization. 8 seems to be stable indefinitely at  $-15^{\circ}$  in pyridine.

Thermal Stability of 4.—A 20-mg sample of 4 was sealed in a thick-walled tube and immersed in an oil bath heated to 170°; the sample melted immediately. Heating was continued for

23.5 hr, and the sample crystallized quickly after being removed from the bath. Glc analysis indicated no decomposition, and the melting point was undepressed.

Photochemistry of 4.—The exploratory procedure was as follows: 15 mg of 4 and 7  $\mu$ l of decane (internal standard) were weighed into a quartz tube (i.d. 5 mm) and exactly 6.0 ml of purified solvent was added. After dissolution was complete the contents were analyzed by glc, degassed, and irradiated using a Srinivasen apparatus fitted with mercury vapor lamps (253.7 nm). After the indicated period, the tubes were again analyzed; the results are given in the text.

Reaction of 4 with 9 (Supplied by Alfa Inorganics).—Following the method of King,<sup>15</sup> a solution of 318 mg (1.29 mmol) of 4 and 238 mg (1.32 mmol) of 9 in 5 ml of octane was heated under nitrogen to 133° for 41.4 hr. The pentane-soluble portion of the product mixture was chromatographed on alumina (activity grade II), eluting first with pentane, then with ether. Unreacted 4 (270 mg, 85%) eluted almost immediately, followed by unreacted 9 (16 mg) a minor band (9.8 mg), then the major product (57 mg crude yield, 79% based on consumed 4). This material was sublimed (87°, 0.05 mm) to yield ca. 30 mg of deep red-orange microcrystalline solid: mp 229–233° (without apparent decomposition);<sup>18</sup> <sup>1</sup>H nmr (deuteriochloroform, internal TMS)  $\delta$  5.09 (s, 5 H), 1.54 (s, 6 H), 1.32 (s, 18 H), 1.27 (s, 6 H); ir (carbon tetrachloride) 2960 (s), 2920 (s), 2865 (m), 1595 (vs), 1484 (m), 1458 (s), 1387 (m), 1369 (m), 1360 (s), 1229 (w), 1190 (w), 1084 (m), 821 (s), 721 cm<sup>-1</sup> (m); mass spectrum (70 eV) m/e 398 (parent and base peak).

Anal. Calcd for C<sub>24</sub>H<sub>35</sub>OCo: C, 72.34; H, 8.85. Found: C, 72.79; H, 9.17.

**Registry No.**—1, 17530-24-4; 2, 1522-16-3; 3, 17553-43-4; 4, 17553-35-4; 5, 17530-17-5; 8, 37439-53-5; 9, 12078-23-8; 12, 37584-03-5; methyllithium, 917-54-4; pyridine, 110-86-1.

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(18) The yield of **12** is unaffected by doubling the amount of dicarbonyl, or by extending the reaction period to 62 hr. Additionally, it is volatile enough to survive passage through an OV-1 gle column at 225°.

# Organophosphorus Enamines. VII. Synthesis and Stereochemistry of Enamine Phosphonates

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Recently we reported a general synthesis of diphenyl and dialkyl 1-alkynylphosphonates  $1.^{2a}$  The literature contains a very limited amount of information on the nucleophilic addition of amines to the carbon-carbon

- (1) The work was initiated at Tulane University, New Orleans, La.
- (2) (a) M. S. Chattha and A. M. Aguiar, J. Org. Chem., 36, 2719 (1971);
- (b) B. C. Saunders and P. Simpson, J. Chem. Soc., 3351 (1963).

<sup>(17)</sup> The contaminating side product must be chemically and physically quite similar to 4, as judged from its gle characteristics and the fact that sublimation and recrystallization only inefficiently separate it from 4. Evidence that it is neither 6 nor 7 comes from the infrared spectrum of impure 4 containing 30% of the contaminant (from concentrated mother liquors), which showed no trace of absorptions in the 1900-2000-cm<sup>-1</sup> region.