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SYNTHESES WITH DIACETYLENIC KETONES

5-MEMBERED RINGS BY ANTI-MICHAEL ADDITION[1]

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Abstract—Syntheses with diphenylethynylketone and di-n-hexynylketone lead to a variety of products deriving from attack at the ketone and/or one or both triple bonds. Adducts with amines, hydrazines, mercaptans, active methylene compounds, and tetraphenylcyclopentadienone were obtained. Among the 6-membered cyclic products, pyridones, and pyrones are expected, while deca-substituted benzophenones are unusual. A novel route to 5-membered rings, e.g. oxo-Δ^2-pyrrolines, thiacyclopentenones (and 3-hydroxythiophenes), and cyclopentenones makes the diethynylketones useful intermediates.

AS PART of an investigation of nonconjugated or "skipped" diynes,[3] we examined the chemistry of the pentadiynones (**1**). These are isomeric with the conjugated 2,4-diynones, of which the naturally occurring capillin, $PhCO(C{\equiv}C)_2Me$, is perhaps the most familiar.[4] Here, we look into the synthetic consequences of flanking a keto

$(RC{\equiv}C)_2C{=}O$ **1** **a**: R = Ph; **b**: R = n-Bu

group with two triple bonds. Perhaps our most interesting finding centers on novel anti-Michael additions to **1**, which yield 5-membered rings.

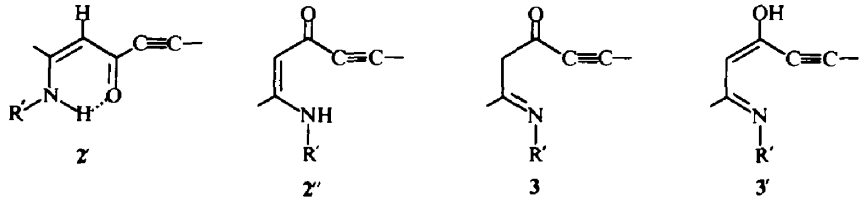
The literature on monoacetylenic ketones is fairly extensive. Attack on the triple bond or at the ketone function by a variety of reagents has been reported, e.g. primary or secondary amines,[5,6] hydrazines,[7,8] semicarbazide,[7] oximes,[8] phenols,[9] thiols,[9] diazo compounds,[8] azides,[10] acidic carbon compounds (e.g. malonic ester),[11] dienes,[12] etc. Appropriate reagents can lead to useful cyclics, e.g. pyrones,[13] pyrazoles,[8] isoxazole,[8] etc.[10] By comparison, the synthetic applications of **1** are largely limited to the contributions of French workers.[14–16] Liang prepared a number of examples of **1**,[14] and Chauvelier and Bardone studied the additions of amines, water and hydrogen sulfide to them.[15,16] Recently, a few reactions of the parent compound, pentadiyne-3-one, were examined,[17,18] In any case, any new information that may be expected in the general area of alkynones should presumably derive from the presence of the second acetylenic group in **1**.

The plan of this paper is to outline the reactions of three groups of reagents with **1**. In each group, there are at least a few unexpected processes *or* unusual products.

Nitrogen compounds and **1**. Chauvelier has given numerous examples of the addition of primary and secondary amines to several pentadiyn-3-ones, under ambient conditions.[15] These adducts (**2**) form readily and tend to be yellow or orange, depending on the substituents.

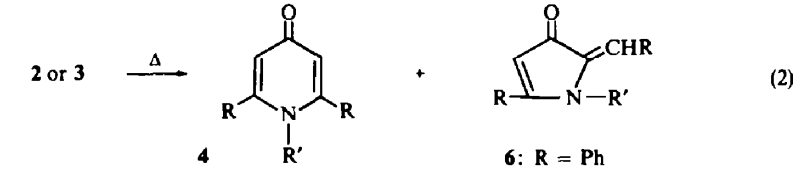
$$1 + R'R''NH \rightarrow RC(NR'R'')=CHCOC{\equiv}CR \qquad \mathbf{2} \qquad (1)$$

Compound **2** is written as a ketone without regard to possible conformational or tautomeric forms, e.g. **2'**, **2''**, 3, 3', when R''=H. One or more of these forms may in fact provide a low energy path for the interconversion of *cis* and *trans*-isomers of **2**,



but we have no evidence on this. In the IR region, the OH and N—H regions are clear, and the CO absorption occurs at ca. 1550 cm^{-1}. In the PMR spectrum, the N—H resonance is found at τ − 1 to −2·5 ppm. Our spectral data are in accord with the ketamine structure (**2**), which is, in fact, the predominant or exclusive one assigned to a variety of other α-β-unsaturated β-ketoamines.[19]

After heating the amine adducts of the pentadiyn-3-ones, e.g. in refluxing xylene, Chauvelier could isolate colorless pyridones (**4**); when diaryldiyn-3-ones were used, she also obtained red or red-orange coproducts which she formulated as hydroxy-naphthalenes, as indicated by **5**, or perhaps the tautomeric keto compounds (not shown). We confirm the observations and the identity of **4**. Since the pyridones (**4**) are unexceptional, they require no further comment. We believe, however, that **5** is an incorrect assignment, and that the colored compounds are actually pyrrolinones (**6**).



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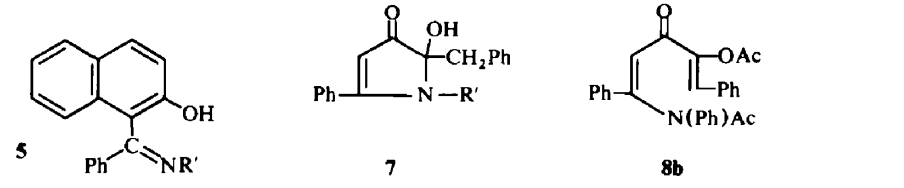


Chauvelier's evidence for the naphthalene structure was plausible at the time. Di-n-pentynylketone did not give red compounds but **1a** did; therefore, an aryl substituent was presumed to enter directly into the reaction. The red color was ascribed to the conjugated system of **5** as well as to possible contributions from the *ortho*-quinoid tautomer. Chauvelier oxidized the compound and obtained benzoic acid, benzanilide, and what, from color tests with phenol and resorcinol, she believed to be *ortho*-phthalic acid. That the compound was insoluble in base and soluble in

acid was perhaps a minor difficulty with structure **5**; its instability would, in fact, make such tests uncertain.

We favor structure **6** over **5** for the red compounds, on the basis of spectral and chemical evidence. Moreover, a number of ketamines closely related to structure **5** have recently been prepared;[19] the Schiff bases of 2-hydroxy-1-naphthaldehyde are white or yellow and their PMR spectra are completely different from those we find for the red compounds. Consistent with its structure, we have found ν_{CO} 1645–1660 cm^{-1} IR bands and two vinylic PMR resonances for several examples of **6**. These reddish compounds are sensitive to both dilute acid and base, discoloring rapidly. When R′ = *p*-dimethylaminophenyl in **6**, the compound forms red needles in recrystallization from acetonitrile, but decomposes when recrystallization from methanol is attempted. This compound gives a brown ferric chloride test. Incidentally, Chauvelier's products of oxidation of the red compound are equally consistent with structure **6**, except for the one questionable color test for phthalic acid.

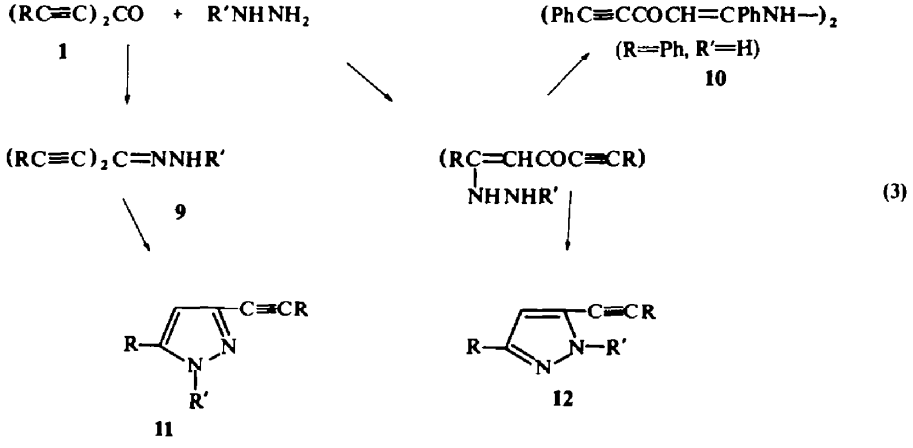
Attempted reductions of **6** with hydrogen over palladium or with sodium borohydride gave moderate to low yields of a hydration product (**7**). This addition of water probably occurred before work up of the product in aqueous acetic acid. In forming **7**, one vinyl proton resonance in the PMR spectrum (τ(PhCH=) $\simeq$ 3·7) is lost from **6**, and an apparent AB pattern and a OH proton resonance show up in **7**. The AB pattern is attributed to a pair of benzylic protons ($J_{CH_2} \simeq 14$ c/s). In one case, **7b**(R′=Ph) was converted with acetyl chloride in pyridine to a derivative (**8b**). Although elemental analysis of **8b** is also consistent with a diacetate structure, the range of IR absorptions in the CO region and the relative simplicity of the PMR spectrum are better represented by the structure we have given. Further work is in progress to clarify the cause of the puzzling hydration and to elucidate the conversion **7** → **8**.

It should be recognized that the formation of **6** (and **7**, **8**) from **1** amounts to a new route to pyrrolinones (oxo-Δ^2-pyrrolines). A few examples of these compounds are known[20,21] and they may be of interest as intermediates.

Comments on the possible mechanism of Eq. 2 may be useful. The lower reactivity of the adduct **2** as compared with **1** in these additions, and also in others to be discussed later, should not be surprising, because of cross conjugation of the nitrogen with the ketone. Although **2′** may be the predominant form of the adduct (**2**), it is convenient to use non-hydrogen-bonded forms in writing a mechanism. Since tautomerization involves proton transfers only, the interconversion of the various forms should be facile, especially at the reaction temperature of ca. 130°, and several may react. In any case, three factors appear to be important in determining whether a 5- or 6-membered ring will form. The normal inductive effect should favor Michael-type addition to yield pyridones (**4**). On the other hand, spatial requirements appear to make the carbon α to the CO group more accessible to the nitrogen, so that anti-Michael formation of **6** should be favored. Finally, when the substituent R on the triple bond is alkyl, the formation of **4** should be favored; when R is Ph, both modes of attack are plausible. Both Chauvelier's and our results seem to indicate that when R is alkyl, **4** is formed exclusively. When R is Ph, both **4** and **6** are formed. These two products appear to come from **1** by independent paths and do not seem to be interconvertible. That they turn up together almost invariably indicates a fine and curious balance.

Hydrazines can attack the keto group or the triple bond of **1**. There are indications

that these paths are competitive, but in acid, the hydrazone is favored, while in neutral or basic solution an amine-type intermediate is formed, as in Eq. 1. Both products may cyclize giving different pyrazoles. We have formulated the modes of attack in general terms in scheme 3, but we do not imply that all of these possibilities can be found for any given reactants. Once any hydrazine species attacks **1** at the triple bond, however, the second triple bond appears to be deactivated towards further reaction with more hydrazine.



(3)

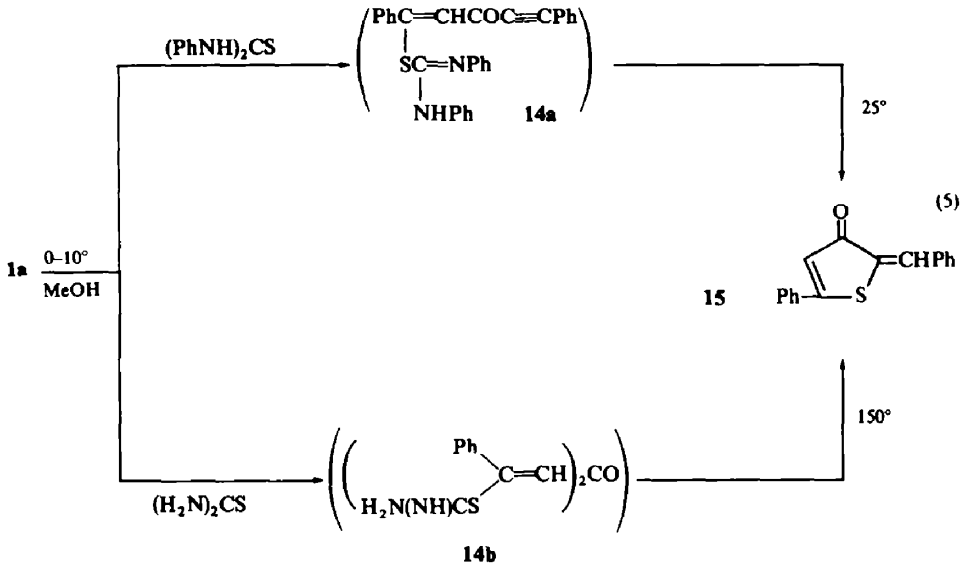
To illustrate the general scheme 3, consider the following. Hydrazine, the most basic of this group of reagents, adds to **1** at or below 0° in ethanol to give the pyrazole (**11**); with **1a**, a red 2:1 diadduct (**10**) was also isolated at 0°. Under similar conditions phenylhydrazine and **1** yield both pyrazoles, **11** and **12**, while 2,4-dinitrophenylhydrazine and **1a** yield **12**. In acidic solution, 2,4-dinitrophenylhydrazine and **1** yield the DNP (**9**), which was rearranged to **11** at elevated temperatures.

Sulphur compounds. On heating **1a** in a sealed tube with hydrogen sulfide in ethanol at 100°, Bardone obtained 1,6-diphenylthiapyrone.[16] Our additions of sulfur compounds were carried out under much milder conditions. Unlike the amines, one mole

$$\mathbf{1a} + \mathrm{RSH} \xrightarrow{\mathrm{MeOH}} (\mathrm{PhC(SR'){=}CH)_2CO} \qquad \mathbf{13} \tag{4}$$

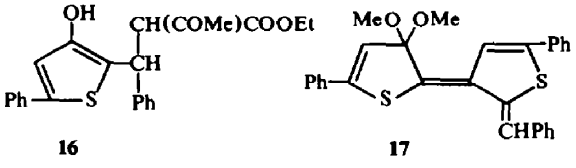
of thiol adds to each side of the ketone giving diadduct. In one case, treatment of **13a** (R = R' = Ph) with strong base gave the corresponding 2,6-diphenylpyrone. Judging by the ease of addition, the thiols, particularly thiols and base, add more rapidly to **1** than do the amines. In the case of *ortho*-aminobenzenethiol, products of thiol addition were obtained in high yield, and no amine adducts could be isolated.

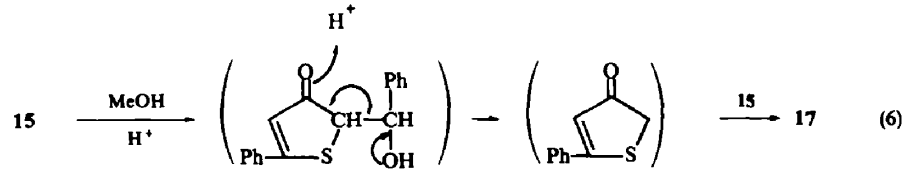
The reaction of pentadiyn-3-one with N,N'-diphenylthiourea was reported to give a yellow adduct of unspecified structure.[17] With both thiourea and N,N'-diphenylthiourea, **1a** yields unstable Michael adducts (**14**) which are readily transformed into the same thiacyclopentenone (**15**):



Since **14a** and **14b** were unstable and usually accompanied by **15**, our structural evidence for them is based on spectral examination. These adducts are readily converted to **15**. It seems unlikely that these anti-Michael adducts (**15**) and Bardone's thiapyrone[16] have a common precursor.

In methanolic sodium hydroxide at 0°, acetoacetic ester added to **15** to give **16**. In acidified methanol **15** is converted to a compound we formulate tentatively as **17**. This could form by a path, which (we speculate) begins with hydration. Condensation



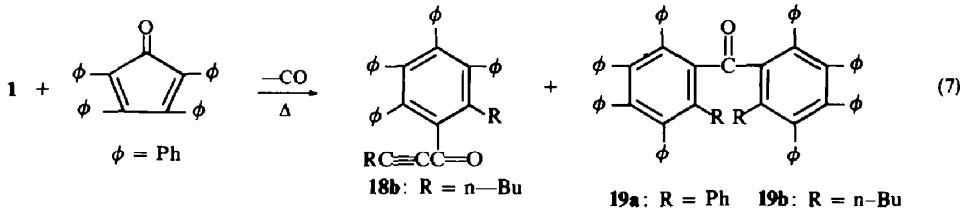


of 2- or 3-hydroxythiophenes with aldehydes is known[22] so that a reverse aldol followed by condensation with more of **15** seems reasonable.

The routes to the 3-thienol (**16**) and thiolen-3-one (**15**) are new; compounds of this type which have attracted recent interest.[23]

Carbon compounds. Diels–Alder reactions of **1** are still of limited application: only the reactions with tetraphenylcyclopentadienone have been successful to date,

but the products are rather interesting. The highly substituted ketones **18** might be expected to be extremely hindered. It was possible, however, to add hydrazine to **18b** and obtain the pyrazole. With regard to decaphenylbenzophenone (**19a**), this is



(7)

unusually unreactive, e.g. to cleavage photolytically or by sodium or potassium hydroxide at elevated temperatures.[24]

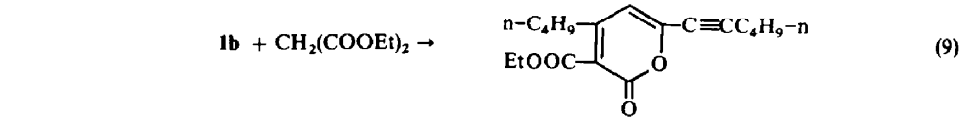
Our preliminary data on the UV spectra of compounds **18** and **19** have several puzzling features, which are now under investigation. Suffice it to say that the *ortho*-butyl groups appear to inhibit the ketonic transition[25a] (D-band) almost completely, and to move the benzenoid transitions to unusually low wave lengths. Unlike the ethynyl ketones where there is positive evidence of carbonyl conjugation, the benzophenones show little, if any, of this. Our UV data for the diethynylketones (**1**) may be compared with those of diethynylmethanes.[3] The data for the *deca*-substituted benzophenones (**19**) may be compared with those of polyphenyls,[25b] polyalkylbenzophenones,[25c] and other *ortho*-substituted benzophenones.[25a]

Carbon nucleophiles attacked at both the triple bond and the keto group. The addition of Grignard reagents to **1** has precedent,[17] although the carbinol (**20**) is new:

$$\mathbf{1b} + C_4H_9C{\equiv}CMgBr \rightarrow (C_4H_9C{\equiv}C)_3COH \qquad (8)$$

20

The formation of pyrones from ketoalkynes and ethyl malonate is also unexceptional:[11]



(9)

21

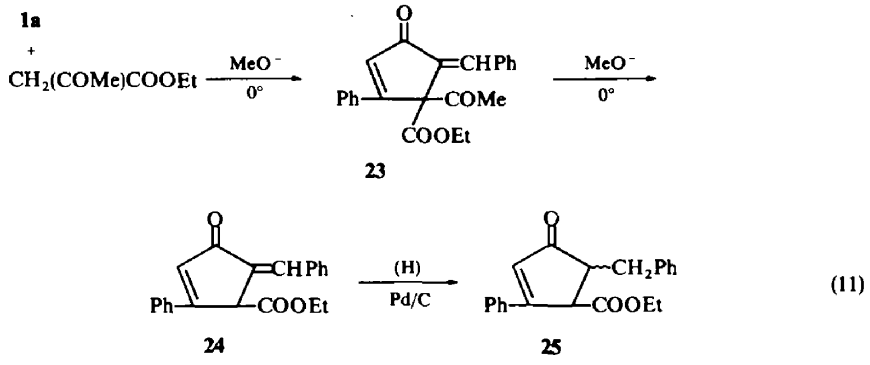
The reactions of malononitrile with **1** gave several products, of which only the keto condensation product was isolated; this is a tetracyanoethene analog, which is now under investigation.

$$\mathbf{1a} + CH_2(CN)_2 \rightarrow (PhC{\equiv}C)_2C{=}C(CN)_2 \qquad (10)$$

22

Stork and Tomasz showed that diethylmalonate added normally in a double Michael addition to a vinyl ethynyl ketone to yield a cyclohexenone intermediate on the way to griseofulvin.[26] By contrast, we found an example of anti-Michael

addition that gives the cyclopentenone (**23**). This product was easily deacylated with base to give **24**, which was reduced to **25**. Our spectral evidence is consistent with the assigned structures **23**, **24** and **25**.



(11)

It is interesting that an active methylene compound and **1** can lead to this variety of products, depending on the initial point of attack and the stability of the intermediates. (We do not yet have an example of a double Michael addition to **1**, which would yield a cyclohexadienone or phenol.) The possibility of geometric isomers, as indicated for **24**, does make for difficulties in product isolation. Nevertheless, it appears that useful syntheses can be developed around **1**. Whether a rationale can be developed for "driving" the reactants along path 9, 10, 11 or the double Michael path remains to be seen.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. NMR spectra were obtained on a Varian A-60 spectrophotometer; TMS served as an internal reference. IR spectra were taken on Perkin–Elmer Model 137 or Beckman IR-8 spectrophotometers. UV spectra were run on Beckman DK-1 and Cary Model 11 spectrophotometers. The chemical shifts τ (ppm), relative to TMS as internal standard, are followed by the splitting pattern: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; where it seems essential, the proton count, the kind of proton and the J value will be indicated in parentheses. Proton counts were taken on all new compounds; except for broad or overlapped resonances, e.g. NH or OH, these counts were usually satisfactory. Elemental analyses were carried out by Micro-Tech, Skokie, Illinois, and M-H-W Laboratories, Garden City, Michigan

Diethynylketones (**1**). The diethynylcarbinols were prepared from the acetylenic Grignard reagent and ethyl formate[14] and then oxidized with CrO_3[7] or MnO_2[27] to the ketones (**1**). Diphenylethynylcarbinol had: mp 84–86°; ν^{KBr} 3280 (OH, broad), 2230 (C≡C) cm^{-1}; τ^{CCl_4} 6·33 d (CH, J = 6·8 c/s), 4·42 d (OH, J = 6·8 c/s), $\tau \sim 2{\cdot}75$. **1a** had: λ_{max}^{EtOH} 228 (ε 19,400), 305 (ε 22,900), 321 (22,800) mμ; ν^{KBr} 1608 cm^{-1} (CO); $\tau^{CCl_4} \sim 2{\cdot}6$; m.p. 64–66° (lit.[15] 63°).

Trideca-5,8-diyn-7-ol had: b.p. 118–120° (0·7 mm), n_D^{25} 1·4763 (lit.[14] b.p. 155–156° (15 mm), n_D^{19} 1·4791); ν 3356 (OH broad), 2928, 2903, 2839 (C—H), 2198, 2222, 2254 (C≡C) cm^{-1}. Trideca-5,8-diyne-7-one (**1b**), prepared in 77% yield, had: b.p. 100–104° (0·2 mm) (lit.[28] b.p. 70° (0·001 mm)); ν 2177 (C≡C), 1663 (CO) cm^{-1}; λ_{max}^{EtOH} 239·5 (ε 13,400), λ_{max}^{EtOH} 250 (ε 13,300) mμ; τ 9·07 m, 8·46 m, 7·66 m.

Amine products

Chauvelier's procedures were generally followed;[15] variations and improvements in her preparative methods were minor. In this section, the pentenynone (**2**) is yellow, the pyridone (**4**) white, and the pyrrolinone (**6**) red to red-orange. New spectral data of the known compounds will serve as a reference.

1-(p-*Chloroanilino*)-1,5-*diphenylpenten*-4-*yn*-3-*one* (**2a**) had m.p. 142–144° (lit.[15] 141·5°); ν^{KBr} 2200 (C≡C), 1550 (CO) cm^{-1}; τ^{CDCl_3} 4·28 s (=CH), ~3·1 (4H, aryl), ~2·67 (10H, aryl), −2·48 s (NH).

N-(p-*Chlorophenyl*) 2,6-*diphenylpyridone* (**4a**) had: m.p. 300–305° dec (lit.[15] m.p. 304°); ν^{KBr} 3055 (=CH), 1620 (CO) cm^{-1}; τ^{CDCl_3} 3·05 s (2H, =CH), 3·07 + 3·43 (4H, aryl, J = 17 c/s), ~2·8 (10H, aryl).

1-(p-*Chlorophenyl*)2-*benzylidene*-5-*phenylpyrrolin*-3-*one* (**6a**) had m.p. 186–188° dec (lit.[15] 194°); ν^{KBr} 3050 (=CH), 1653 (CO), 1542 (C=C) cm^{-1}; τ^{CDCl_3} 4·23 s, 3·71 s, ~2·75 m (12H, aryl), ~2·0 m (2H, aryl).

1-p-*Chlorophenyl*-5-*phenyl*-2-(α-*hydroxybenzyl*)2-*pyrrolin*-3-*one* (**7a**). Excess $NaBH_4$ (10 mg) in a solvent of 2-propanol (5 ml) and THF (3 ml) was added to **6a** (0·3 g) in THF (5 ml) at 0°. After 15 min at ca. 0°, the mixture was poured into a mixture of ether (50 ml), water (50 ml) and glacial AcOH (2 ml). The ether layer was worked up to give a few mg of a *hydration* product which had m.p. 198–199°, from MeOH; ν^{KBr} 3030, 1679 (CO). The structural assignment was made by analogy with the results of similar reactions, since PMR data were not obtained. (Found: C, 73·84; H, 4·55. $C_{23}H_{18}NO_2Cl$ requires: C, 73·49; H, 4·82%).

1-*Anilino*-1,5-*diphenylpenten*-4-*yn*-3-*one* (**2b**) had m.p. 143–145° (lit.[15] m.p. 143°); ν^{KBr} 2190 (C≡C), 1555 (CO) cm^{-1}; τ^{CCl_4} 4·43 (=CH), ~2·7 (aryl).

1,5-*Diphenyl*-2-*benzylidene*-2-*pyrrolin*-3-*one* (**6b**) had m.p. 192–194° (lit.[15] 198°); ν^{KBr} 1645 (CO), 1548, 1377 cm^{-1}; τ^{CDCl_3} 4·29 s (=CH), 3·73 (=CH), 3·15 m, 2·85 m, and 2·0 m (aryl).

1,5-*Diphenyl*-2-(α-*hydroxybenzyl*)2-*pyrrolin*-3-*one* (**7b**). To compound **6b** (3 g) in THF (25 ml) at 0° was added a cooled soln of $NaBH_4$ (0·4 g) in abs EtOH (10 ml). The mixture was kept at 0° for 7 min and quenched in water (50 ml) plus glacial AcOH (2 ml) plus ether (50 ml). A yellow solid was obtained in 25% yield from the ether layer; it had m.p. 198–199°, from MeOH; ν^{KBr} 3160 (OH), 3050 (=CH), 1648 (CO) cm^{-1}; $\tau^{pyridine}$ ~6·25 (2H, J = 14 c/s), 5·45 (OH, broad), 4·43 s (=CH). This material **7b** appears to be a hydration product, but because of an unsatisfactory elemental analysis, its identity is in doubt. A derivative (**8b**) was prepared as follows: Ac_2O (9 ml), pyridine (0·5 ml), AcCl (2 ml) and **7b** were allowed to stand ca. 12 hr. Work up yielded a yellow solid (0·05 g), which had: m.p. 206–208° from CCl_4; ν^{KBr} 1747, 1673, 1651, 1634, 1298, 1204 cm^{-1}; τ^{CDCl_3} 7·84 s (3H), 7·66 s (3H), 3·00 s (1H), ~2·7 m (aryl). As pointed out earlier (following Eq. 2) we suppose this solid is 1-(N-*phenylacetamido*)-4-*acetoxy*-1,5-*diphenylpentadien*-3-*one*. (Found: C, 76·30; H, 5·31. $C_{27}H_{23}NO_4$ requires: C, 76·22; H, 5·57%).

1-(N,N-*Dimethyl*-p-*phenylenediamino*)1,5-*diphenylpenten*-4-*yn*-3-*one* (**2d**). *p*-N,N-Dimethylphenylenediamine (1 ml, 0·0066 mole) was added to **1a** (1 g, 0·004 mole) in MeOH (20 ml) at 0° or 25°. A red-orange solid (1·4 g or 88% yield) precipitated, m.p. 185–186°, from MeOH. It had: ν^{KBr} 2880, 2790 (CH_3), 2200, 2190 (C≡C), 1600, 1582, 1555 (CO), 1538, 1518 cm^{-1}; τ^{CDCl_3} 7·17 s (6H), 4·38 s (1H), 3·28 + 3·57 (4H, J ~ 9 c/s), ~2·7 (10H, aryl); τ^{DMSO} ~2·41 (aryl), −1·71 (NH), −3·2 (NH, broad). (Found: C, 81·71; H, 6·18. $C_{25}H_{22}N_2O$ requires: C, 81·93; H, 6·05%).

N-(p-N',N'-*Dimethylaminophenyl*)2,6-*diphenylpyridone* (**4d**). Compound **2d**, (5 g), was kept at the m.p. in an oil bath for ca. 1 min. Benzene (70 ml) was added to the hot melt and the soln was allowed to cool. The pyridone (**4d**) was recrystallized from Skelly B–benzene (40:60) and EtOH in 15% yield. Compound **2d** (6 g) was also heated at reflux in xylene (100 ml) for 3 hr. On cooling, some pyridone separated. The white solid (0·2 g in 3% yield) had m.p. 289–290°; ν^{KBr} 3060, 2883, 2800, 1625 (CO), 1515 cm^{-1}; τ^{CCl_4} 7·18 s (6H), 3·76 s, ~2·9 m. (Found: C, 82·02; H, 6·08. $C_{25}H_{22}N_2O$ requires: C, 81·93; H, 6·05%).

1-(p-N',N'-*Dimethylaminophenyl*)2-*benzilidene*-5-*phenylpyrrolin*-3-*one* (**6d**). The filtrate from the preceding preparation was evaporated and the residue washed with MeOH to remove **4d**. The remaining solid, which decomposes in hot alcohol and is sensitive to acid, was recrystallized from acetonitrile to m.p. 178–180° in 40% yield (2·4 g). It had: ν^{KBr} 1657 (CO), 1540 cm^{-1}; τ^{CDCl_3} 7·15 s (6H), 4·37 s (=CH), 3·75 s (=CH), 2·9 + 3·33 (4H, J = 18 c/s), 2·87 m + 2·1 m (aryl). (Found: C, 82·22; H, 6·13. $C_{25}H_{22}N_2O$ requires: C, 81·93; H, 6·05%).

1-(p-N,N-*Dimethylphenyl*)2-(α-*hydroxybenzyl*)5-*phenyl*-2-*pyrrolin*-3-*one* (**7d**). A rapid hydrogenation of **6b** (1 g) in ether–AcOEt (80:20, 250 ml) over 5% Pd–C (0·5 g) was attempted. Work up yielded yellow crystals of a hydration product (0·45 g), which had m.p. 160–161° dec, from acetone; ν^{KBr} 3190 (OH), 2800–2900 (Me), 1640 (CO), 1517 (C—N), 1126 cm^{-1}; τ^{CDCl_3} 7·08 s (NCH_3), ~6·7 (2H, CH—CHO), 5–6 (OH, broad), 4·61 s (=CH), ~3 m (14H). (Found: C, 78·20; H, 6·31. $C_{25}H_{24}N_2O_2$ requires: C, 78·10; H, 6·29%).

o-*Aminoanilino*-2-*benzilidene*-5-*phenylpyrrolin*-3-*one* (**6e**). *o*-Phenylenediamine (0·228 g) and **1a** (0·5 g) were mixed. In a few min, the crystals that formed were filtered and vacuum dried. The orange solid (0·5 g, 64% yield) was recrystallized from EtOH and stored under N_2. It had m.p. 159–160°; ν^{KBr} 3440, 3300, 3190 (NH, broad), 2200, 2190 (C≡C), 1550 (CO) cm^{-1}. τ^{CCl_4} 6·77, 4·31, ~2·89, −2·1 (broad, NH). (Found: C, 81·33; H, 5·58. $C_{23}H_{18}N_2O$ requires: C, 81·63; H, 5·36%).

1-(p-*Methylanilino*)1,5-*diphenylpenten*-4-*yn*-3-*one* (**2f**) had m.p. 144–145° (lit.[15] 140°); ν^{KBr} 2180 (C≡C), 1560 (C=O), 1325 cm^{-1}; τ^{CDCl_3} 7·78 s (3H), 4·33 s (=CH), ca. 2·7–3·0 (aryl), −2·5 s (NH).

1-p-*Tolyl*-2-*benzylidene*-5-*phenylpyrrolin*-3-*one* (**6f**) had m.p. 164–166·5° (lit.[15] 170°); ν^{KBr} 1650 (C=O), 1510, 1535, 1370 cm^{-1}; τ^{CDCl_3} 7·68 s (3H), 4·26 s (=CH), 3·71 s (=CH), ~1·8 + 2·7 + 3·0 (14H, aryl).

1-(p-*Tolyl*)2-(α-*hydroxybenzyl*)5-*phenyl*-2-*pyrrolin*-3-*one* (**7f**). Rapid hydrogenation of **6f** (5 g) in $CHCl_3$–ether (30:70, 250 ml) over 5% Pd–C (1 g) was attempted. Work up yielded a yellow hydration product (0·5 g), which had m.p. 154–158° dec, from ether–heptane; ν^{KBr} 3210 (OH), 1646 (CO), 1510, 1222 cm^{-1}; τ^{CDCl_3} 7·71 s (Me), ~6·9 (2H, J = 13·5 c/s), 5·95 (OH, broad), 4·67 s (=CH), ~2·8 m (14H). (Found: C, 81·09; H, 5·87; N, 4·17. $C_{24}H_{21}NO_2$ requires: C, 81·10; H, 5·96; N, 3·94%).

p,p'-*Bis*-(*anilino*-1,5-*diphenylpentene*-4-*yn*-3-*one*)*methylene* (**2g**). A soln of **1a** (1 g) in MeOH (5 ml) and *p,p'*-methylenedianiline (0·4 g) in MeOH (15 ml) were mixed and warmed until crystals began to form. The yellow-orange solid (0·5 g) had m.p. 178–179°, from EtOH; ν^{Nujol} 2195 (C≡C), 1600 sh, 1590, 1560, 1540 cm^{-1}; τ^{CCl_4} 6·3 (CH_2), 4·6 (=CH), ~3·28 (aryl), ~2·38 (aryl), −1·24 (NH). (Found: C, 85·40; H, 5·38. $C_{47}H_{34}N_2O_2$ requires: C, 85·68; H 5 2%).

1-(*Benzylamino*)1,5-*diphenylpentene*-4-*yn*-3-*one* (**2h**). Benzylamine (0·232 g) was added to a warm soln of **1a** (0·5 g) in MeOH (5 ml). The soln was warmed for ca. 1 min on the steambath, then the solvent was removed under vacuum. The yellow solid had m.p. 131–132°, from benzene–Skelly B; ν^{KBr} 2190 (C≡C), 1595 (CO) cm^{-1}; τ^{CCl_4} 5·65 (CH_2), 4·67 (=CH), ~2·75 (aryl), −1·25 (NH). (Found: C, 85·48; H, 5·83. $C_{24}H_{19}NO$ requires: C, 85·47; H, 5·63%).

1-(*Dicyclohexylamino*)1,5-*diphenylpentene*-4-*yn*-3-one (**2i**). Compound **1a** (0·345 g) was added to a warm soln of dicyclohexylamine (0·5 g) in MeOH (6 ml). The soln was warmed for ca. 1 min on the steam bath, then the solvent was removed under vacuum. The yellow solid (0·5 g) had: m.p. 153·5–154·5°, from Skelly B–benzene; ν^{KBr} 2190, 2175 (C≡C), 1595 (CO) cm^{-1}; τ^{CCl_4} ~7·5 m (11H, broad), 4·35 (=CH), ~2·87 (aryl). (Found: C, 85·48; H, 5·83. $C_{24}H_{19}NO$ requires: C, 85·47; H, 5·63%).

5-(p-N,N-*Dimethylaminoanilino*)*trideca*-5-*ene*-8-*yn*-7-*one* (**2j**). Freshly distilled *p*-N,N-dimethylaniline (0·36 g), **1b** (0·5 g) and MeOH (5 ml) were mixed and allowed to stand for 3 days. The soln was worked up to give a yellow solid, from petroleum ether, in 69% yield. The solid had m.p. 60–62°; ν^{KBr} 2200 (C≡C), 1600 sh, 1580 (broad) cm^{-1}; τ^{CCl_4} ~9·05 m (6H), 8·57 m (8H), 7·8 m (4H), 7·1 (6H), 4·86 s (=CH), ~3·26 m, −2·29 s (NH). (Found: C, 77·10; H, 9·29. $C_{21}H_{30}N_2O$ requires: C, 77·26; H, 9·26%).

4-(N,N-*Dimethylaminophenyl*)2,6-*di*-n-*butylpyridone* (**4j**). Compound **1b** (2 g, 0·01 mole), *p*-N,N-dimethylaniline (1·43 g, 0·01 mole) and toluene (5 ml) were heated under N_2 at reflux for 59 hr. The dark product was worked up and partially purified by column chromatography. The first crops of solid, eluted with benzene and EtOH, probably contained some open chain adduct and starting amine. Crystals from the mother liquor (0·7 g) were also impure, but recrystallization from toluene, hexane–benzene, and hexane–CCl_4 yielded a white solid, m.p. 116–118°; ν^{KBr} 1628 (CO) cm^{-1}; τ^{CCl_4} ~9·2 m (6H), ~8·7 m (8H), 7·9 m (4H), 7·3 (impurity), 6·9 (6H), 4·1 (=CH), ~3·1 m (aryl). (Found: C, 76·82; H, 9·22. $C_{20}H_{30}N_2O$ requires: C, 77·20; H, 9·26%).

Hydrazine products

2,4-*Dinitrophenylhydrazone of* **1a** (**9a**). Compound **1a** (0·5 g) and 2,4-dinitrophenylhydrazine (0·233 g) were mixed in MeOH (30 ml) and conc HCl (1 ml). The mixture was heated for ca. 3 min at reflux temp, when crystals separated. The orange solid (0·3 g), from toluene, had m.p. 205–206°; ν^{KBr} 3220 (NH), 2185 (C≡C), 1600 (C=N) cm^{-1}; τ^{xylene} −2·1 s (NH). (Found: C, 67·15; H, 3·58. $C_{23}H_{14}N_4O_4$ requires: C, 67·29; H, 3·43%).

2,4-*Dinitrophenylhydrazone of* **1b** (**9b**). This was prepared in almost quantitative yield from **1b** and 2,4-dinitrophenylhydrazine in acidified alcohol. The yellow solid had: m.p. 87·3–87·5°, from EtOH; ν^{KBr} 3230 (NH), 2210 (C≡C), 1604 (C=N) cm^{-1}; τ^{CCl_4} 8·93 m (6H), 8·38 m (8H), 8·17 m (4H), 2·13 d (1H, J ~ 1·2 c/s), 1·73 q (1H, J ~ 1·2, 4·7 c/s), 1·00 d (1H, J ≃ 1·2 c/s), −1·83 s (1H). (Found: C, 61·46; H, 6·17. $C_{19}H_{22}N_4O_4$ requires: C, 61·61; H, 5·99%).

1-(2,4-*Dinitrophenyl*)3-*phenylethynyl*-5-*phenylpyrazole* (**11a**). DNP **9a** (0·12 g) was heated in boiling DMSO (3 ml) for 2 min, cooled, and worked up. Compound **11a** (0·1 g) had m.p. 205–206°, from EtOH; ν^{KBr} 3090, 2220 (C≡C), 1605, 1530, 1540, 1343 cm^{-1}; τ^{CDCl_3} 3·3 s (=CH), 1·7–2·3 (13H, aryl). (Found: C, 67·45; H, 3·30. $C_{23}H_{14}N_4O_4$ requires: C, 67·29; H, 3·43%).

1-(2,4-*Dinitrophenyl*)5-*phenylethynyl*-3-*phenylpyrazole* (**12a**). Compound **1a** (1·0 g) in MeOH (20 ml) was added to 2,4-dinitrophenylhydrazine (0·86 g) in boiling MeOH (80 ml). The soln was boiled until all of the hydrazine dissolved, then slowly evaporated. The oily solid was recrystallized from MeOH–EtOAc.

The crystals (0·43 g) were yellow and had m.p. 169·5–171°. The m.p. and NMR spectrum of this pyrazol were identical with that of a sample prepared by a different method, that is from the DNP of 1,5-diphenylpentadiyn-1-one, m.p. 220–222° dec (lit.[4] 225° dec). A soln of this hydrazone (87 mg) in DMSO was boiled for ca. 1 min, cooled and worked up. The yellow solid (67 mg) had m.p. 170–171·2° ν^{KBr} 2215 (C≡C), 1605, 1530, 1342; τ^{CDCl_3} 2·99 s (1H), ~1·2 m + 2·2 m + ~2·7 m (aryl). (Found: C, 67·15; H, 3·58. $C_{23}H_{14}N_4O_4$ requires: C, 67·29; H, 3·43%).

1-*Phenyl*-5-(1-n-*hexynyl*)3-n-*butylpyrazole* (**12b**) and 1-*phenyl*-3-(1-n-*hexynyl*)-5-n-*butylpyrazole* (**11b**). Di-n-hexynylketone (2 g, 0·01 mole) and EtOH (10 ml) were cooled to −10° under N_2. Freshly distilled phenylhydrazine (3·4 g, 0·03 mole) was added slowly (30 min) to the stirred soln. After 20 min longer at −10°, the soln was allowed to stand overnight at ca. 25°. After working up the product and discarding material insoluble in hexane, we obtained a colored oil (2·9 g), which appeared to contain both pyrazoles (**11b** and **12b**). Column chromatography on alumina followed by another pass of the hexane fraction, and removal of the solvent from the leading eluate (hexane), yielded pyrazole **12b**, n_D^{25} 1·5506, λ_{max}^{EtOH} 254 (ε 1·62 × 10⁴), λ_{min}^{EtOH} 229 mμ (ε 4·08 × 10³). A second pass of the benzene eluate on alumina yielded 5 fractions of which the fourth, hexane–benzene (1:2) contained pyrazole **11b**, n_D^{27} 1·5534, λ_{max}^{EtOH} 254 (ε 1·42 × 10⁴), λ_{min}^{EtOH} 232 mμ (ε 8·96 × 10³). Although the IR spectra of these compounds differed in detail, we did not find them useful for structure assignment; both had: ν^{neat} 2240 (weak) and a series of medium to strong bands near 1601, 1544, 1505, 1465, 1429, 1377 cm^{-1}. The PMR spectra and proton counts were diagnostic, particularly τ 3·7 and 3·9, which appeared together in the crude product and separated into different fractions, as purification progressed. Pyrazole **12b** had: τ^{CCl_4} 9·0 m, 8·5 m, 7·7 t + 7·4 t (4H), 3·7 (=CH), ~2·7 m + ~2·2 m (5H); this pattern seems to be consistent with aryl on N adjacent to the triple bond. Pyrazole **11b** had 9·0 m, ~8·5 m, ~7·5 m, 3·9 s (=CH), 2·7 m (5H); this pattern seems to be in accord with the aryl group on N adjacent to the Bu group. Admittedly, the structural assignment is uncertain; it is based on the notion that in a comparison of the pyrazoles, the ethynyl group of **12b** lowers τ for the vicinal aryl protons, and the aryl group of **11b** lowers τ for the vicinal α-methylene protons. The relative magnitudes of τ (=CH) for the ring protons are also consistent with those of the τ values for **11a** and **12a**, whose structures are known. (Found for pyrazole **12b**: C, 81·35; H, 8·56. Found for pyrazole **11b**: C, 80·54; H, 8·82. $C_{19}H_{24}N_2$ requires: C, 81·38; H, 8·63%).

5-*Phenyl*-3-*phenylethynylpyrazole* (**11c**). Hydrazine hydrate was added to **1a** (0·5 g) in EtOH until no further red color formed. The soln was warmed on the steam bath ca. 1 min, cooled, and worked up. Chromatography of the oily product on alumina yielded a yellow solid, m.p. 110–111°, from MeOH–water. It had ν^{Nujol} 3200, 3131, 1590 (CO), 1560 cm^{-1}; τ^{CCl_4} 3·28 s (=CH), ~2·5 m (10H), −3·5 (NH, broad). (Found: C, 83·86; H, 5·05. $C_{17}H_{12}N_2$ requires: C, 83·58; H, 4·95%).

1,2-Bis-(1,5-*diphenyl*-3-*oxopenta*-1-*en*-4-*ynyl*)-*hydrazine* (**10**). Compound **1a** (1 g) was dissolved in MeOH and kept below 10°. Hydrazine hydrate (ca. 1 ml) was added until no further red color formed. Stirring and scratching promotes the formation of impure powdery red crystals (0·08 g after several recrystallizations from MeOH). The pure red solid had m.p. 182–183° dec, from MeOH–benzene; ν^{KBr} 2210 (C≡C), 1617, 1555, 1320; τ^{CDCl_3} 4·49 s (2H, =CH), ~2·6 m (20H, aryl), −2·6 (1-2H, NH). (Found: C, 82·89; H, 5·23. $C_{34}H_{24}N_2O_2$ requires: C, 82·90; H, 4·92%).

3-*Butyl*-5-(1-*hexynyl*)*pyrazole* (**11d**). Compound **1b** (1 g) and EtOH (5 ml) were cooled in a 3-necked flask, fitted with a dropping funnel, condenser, and gas inlet tube, to −10°. The system was flushed with N_2, and freshly distilled dry hydrazine (1 g) was added slowly. The temp was kept at ca. 10° for 30 min and at 25° overnight. Work up of the product yielded a white solid, m.p. 28–30°, from n-hexane (at −70°), b.p. 133–136° (0·01 mm). It had: ν^{neat} 3185, 3200 (NH) cm^{-1}; τ^{CCl_4} 9·1 m (6H), 8·4 m (8H), 7·6 m (2H), 7·3 m (2H), 4·1 s (=CH), −2·5 s (NH). (Found: C, 76·17; H, 9·84. $C_{13}H_{20}N_2$ requires: C, 76·42; H, 9·86%).

Sulfur products

Aryl thiols and **1a** were warmed for ca. 30 min in methanolic base. The solns were then worked up to give adducts of two moles of thiol to **1**.

1,5-*Diphenylthio*-1,5-*diphenylpentadien*-3-*one* (**13a**) had m.p. 173–173·5°; ν^{Nujol} 1610 (CO), 1540; τ^{CCl_4} 3·47 s (2H, =CH), ~2·94 m (10H, aryl). (Found: C, 77·41; H, 5·08. $C_{29}H_{22}OS_2$ requires: C, 77·29; H, 5·03%).

Compound **13a** (2 g) was heated with KOH (4 g) in EtOH (50 ml) at reflux for 30 min and then worked up. The crude product was purified by column chromatography on alumina. Apart from an oil which was not identified, we obtained white 2,6-diphenylpyrone (0·1 g), m.p. 140–142° (lit.[15] 139–140°), whose picrate had m.p. 184–186° (lit.[29] 181–183°).

1,5-*Di*-p-*tolylthio*-1,5-*diphenylpentadien*-3-*one* (**13b**). By the same procedure as for **13a**, a solid, m.p. 177–178·0° was obtained. It had: ν^{Nujol} 1612, 1540, 1115 cm^{-1}; τ^{CCl_4} 7·85 s (6H), 3·48 (2H, =CH), $\tau \sim 2·9$ m (18H, aryl). (Found: C, 77·91; H, 5·51. $C_{31}H_{26}S_2O$: C, 77·78; H, 5·47%).

1,5-*Bis*-(o-*aminobenzenethio*)1,5-*diphenylpentadien*-3-*one* (**13c**). Work up yielded a yellow solid, m.p. 166–168·5° dec from benzene–EtOH. It had: ν^{Nujol} 3420, 3330, 1605 (CO); τ^{DMSO} 4·83 (2H), 3·32 (2H), ~3·0 (18H, aryl). (Found: C, 72·58; H, 5·22. $C_{24}H_{24}N_2OS_2$ requires: C, 72·49; H, 4·99%).

1,5-*Bis*-(o-*aminobenzenethio*)1,5-*di*-n-*butylpentadien*-3-*one* (**13d**). Work up yielded a yellow solid, m.p. 141–154° dec, from benzene. It had: ν^{KBr} 3463, 3440, 3354, 1603 (CO, broad), 1545 (broad) cm^{-1}; τ^{CCl_4} ~9·3 m (6H), ~8·7 m (8H), ~7·8 m (4H), 5·8 s (NH_2, broad), 3·6 (=CH), ~2·6 m + ~3·2 m (aryl). (Found: C, 68·31; H, 7·37; N, 6·27; S, 14·4. $C_{25}H_{32}S_2N_2O$ requires: C, 68·1; H, 7·31; N, 6·35; S, 14·5%).

2-*Benzylidene*-3-*keto*-5-*phenyl*-1,2-*dihydrothiophene* (**15**). The monoadduct (**14a**) of diphenylthiourea and **1a** can be obtained by mixing the reagents in methanol and filtering it off. On standing, this solid turns yellow rapidly as it forms **15**. Because of its low solubility and stability, no PMR spectrum was taken; it had: ν^{KBr} 3255 (NH), 2210, 2180 (C≡C), 1637 (CO), 1584 (C=N), 1313 cm^{-1}. The diadduct (**14b**) of thiourea and **1a** was obtained in the same way. **14b** decomposed when it was recrystallized from solvents, or when its m.p. was sought. Although it appears to be stable at ca. 25°, it is sparingly soluble in the common solvents. It had: ν^{KBr} 3441 (NH), 3100 (NH_2), 1690 (CO), 1340, 760 cm^{-1}. **1a** (2 g) in methanol (75 ml) at ca. 0° was added to a solution of thiourea (0·66 g) in MeOH–water (V/V 25/10) at ca. 0°. After 15 min, water (50 ml) was added to the soln, the mixture was brought to a boil and then allowed to cool. The solid was filtered off and washed with cold MeOH. Alternatively, **14b** can first be prepared by rapid mixing of the reagents, followed by washing with MeOH. This solid can be rearranged cleanly in DMSO or in boiling MeOH (1 hr). Compound **15** (1·2 g or 52% yield) had: m.p. 142–144°, from MeOH; ν^{KBr} 1654 (CO), 1545, 1248, 1175 cm^{-1}; τ^{CCl_4} 3·37 s (ring H), ~2·79 m (aryl), 2·33 s (=CH). (Found: C, 77·37; H, 4·54. $C_{17}H_{12}OS$ requires: C, 77·24; H, 4·57%).

2-(1-*Phenyl*-2-*carbethoxy*-3-*ketobutyl*)3-*hydroxy*-5-*phenylthiophene* (**16**). Compound **15** (5 g) in EtOH (150 ml), NaOH (0·75 g) in aqueous EtOH (35 ml), acetoacetic ester (3 g) were mixed and allowed to stand for 15 min. The soln was acidified and worked up. The solid (4·1 g) had m.p. 136–138°, from MeOH; ν^{KBr} 3435 (OH), 1737 (CO), 1704 (CO) cm^{-1}; τ^{CDCl_3} 9·02 t (3H, J = 7 c/s), 8·32 s (3H), 6·98 d (1H, J = 12 c/s), 6 q (2H, OCH_2, J = 7 c/s), ~6·05 (OH, broad), 5·47 d (1H, J = 12 c/s), 3·12 s (=CH), $\tau \sim 2·73$ m (10H, aryl). (Found: C, 69·7; H, 5·63; S, 8·03. $C_{23}H_{22}O_4S$ requires: C, 70·06; H, 5·62; S, 8·12%).

2,3,2',3'-*Tetrahydro*-5,5'-*diphenyl*-3,3-*dimethoxyl*-2'-*benzilidene*-$\Delta^{2,3'}$-*biothiophene* (**17**). Compound **15** (3 g) and conc H_2SO_4 (30 ml) in MeOH (400 ml) were boiled for 1 hr; water was added to maintain the volume and precipitate the product. The ketal (1·7 g) had m.p. 174–175° dec, from acetonitrile, and is sensitive to light, darkening in a few days. It had: ν^{KBr} 2955, 2930, 2900, 2850, 1560, 1380, 1109, 1090 cm^{-1}; τ^{CDCl_3} 6·28 (6H), 3·85 s (=CH, ring), 2·97 s (=CH), ~2·7 (aryl). One of the thienyl proton resonances is presumably overlapped in the aryl region. (Found: C, 74·51; H, 5·23; S, 13·36. $C_{29}H_{24}O_2S_2$ requires: C, 74·23; H, 5·16; S, 13·68%).

Carbon compounds

1-(1-*Butyl*-2,3,4,5-*tetraphenyl*)*hept*-2-*yn*-1-*one* (**18b**). Compound **1b** (0·5 g, 0·00265 mole) and tetracyclone (2·0 g, 0·0053 mole) in *o*-dichlorobenzene (10 ml) were heated at reflux (ca. 179°) under N_2. Gas evolution was vigorous, at first. After 24 hr, the soln was still purple because of unreacted tetracyclone. The solvent was removed under vacuum and the residue treated with maleic anhydride (0·52 g, 0·0053 mole) and triethylene glucol dimethyl ether (10 ml). After heating to reflux the purple color was removed. The tan residue was cooled, treated with water and base. The desired product had: m.p. 173–174·5°, from petroleum ether; λ^{EtOH} 304 (ε 4·3 × 10^3), 279 (ε 1·17 × 10^4), and 224 (ε 7·05 × 10^4) mμ, where these were shoulders on a rising absorption curve; ν^{KBr} 2200 (C≡C), 1650 (CO) cm^{-1}; τ^{CCl_4} ~9·14 m, 8·66 m, 7·9 m, 7·5 m, ~2·9–2·8 m. (Found: C, 90·12; H, 7·07. $C_{41}H_{38}O$ requires: C, 90·07; H, 7·00%).

3-*Butyl*-5-(1-*butyl*-2,3,4,5-*tetraphenylphenyl*)*pyrazole*. Compound **18b** (0·1 g), hydrazine hydrate (1 g), EtOH (5 ml) and one drop of dil H_2SO_4 (0·5 M) were mixed and allowed to stand overnight. Work up of the mixture yielded a white solid, m.p. 204–207°, from hexane. (Found: C, 87·84; H, 7·59. $C_{41}H_{40}N_2$ requires: C, 87·81; H, 7·19%).

Decaphenylbenzophenone (**19a**). Compound **1a** (0·5 g, 0·002 mole) and tetracyclone (1·536 g, 0·004 mole) were heated at reflux in *o*-dichlorobenzene (11 ml) overnight. The product was precipitated out with Skelly B. It had m.p. 411–412°, from toluene; ν^{KBr} 1675 (CO); $\lambda_{max}^{95\%EtOH}$ 239 mμ (ε, 57,000), 270 sh (ε 21,000), 396 sh (ε 9500). (Found: C, 93·21; H, 5·13. $C_{73}H_{50}O$ requires: C, 92·96; H, 5·34%).

o,o', *Di-n-butyloctaphenylbenzophenone* (**19b**). Compound **1b** (1 g, 0·0052 mole), tetracyclone (3·66 g, 0·0104 mole), and tetraethylene glycol dimethyl ether (30 ml) were heated slowly to reflux (275°) temp under N_2. After 5–6 hr, maleic anhydride (0·5 g) was added and heating was continued for 1 hr more. The product was worked up from aqueous alkali to give a white solid, m.p. 299·5–3·1·5°, from benzene, in 32% yield. (This compound melted and resolidified in the range 180–200°, remaining white until the m.p. at 300°). It had: ν^{KBr} 1665 (CO) cm^{-1}; λ^{EtOH} 302 (ε 1·4 × 10^4), 278 (ε 1·7 × 10^4) and 227 (ε 1·06 × 10^5) mμ, where these were shoulders on a rising absorption curve. (Found: C, 91·36; H, 7·19. $C_{69}H_{58}O$ requires: C, 91·76; H, 6·47%). A second white solid, m.p. 160–163°, ν_{CO} 1687 cm^{-1} and no $\nu_{C\equiv C}$ was found in the mother liquors, but was not investigated further.

Tri-n-hexynylcarbinol (**20**). EtMgBr, prepared from Mg (0·6 g) and EtBr (3·3 g) in ether (20 ml), was treated with 1-hexyne (2 g) in ether (5 ml) in a N_2 atm. To this soln kept at 5°, **1b** (1·9 g) in ether (10 ml) was added, then stirred for 6 hr at ca. 25°. The mixture was worked up in the usual way and the product (1·7 g) collected by vacuum distillation. In the alternate method, 1-hexynylmagnesium bromide in ether (250 ml) was prepared from 1-hexyne (41 g, 0·5 mole) under N_2. To this soln, cooled at ca. 0°, diethyl carbonate (19·7 g, 0·17 mole) in ether (100 ml) was added at a rate sufficient to maintain refluxing of solvent. The reaction mixture was stirred at ca. 25° for 48 hr. Work up and distillation gave: a fraction (17·6 g), b.p. 138–145° (0·05 mm); n_D^{34} 1·4758; ν^{neat} 3300–3600 (OH), 2220 (C≡C) cm^{-1}; τ 9·08 m, 8·51 m, 7·78 m, 6·88 s. (Found: C, 83·76; H, 10·58. $C_{19}H_{28}O$ requires: C, 83·76; H, 10·36%).

3-Carbethoxy-4-n-butyl-6-(1-n-hexynyl)2-pyrone (**21**). Compound **1b** (2·0 g, 0·01 mole), diethylmalonate (1·96 g, 0·012 mole), EtOH (20 ml) and EtONa (from 0·012 g Na and 1 ml EtOH) were mixed under N_2. After the exothermic reaction was over, the mixture was heated at reflux for 3 hr, cooled, acidified with AcOH and worked up. Vacuum distillation of the oil gave a fraction: b.p. 175–179° (0·015 mm), ν^{neat} 2220 (C≡C), 1720 (CO, broad), 1618 (C=C) cm^{-1}; τ^{CCl_4} ~9·1 (6H), ~8·5 m (11H), ~7·5 m (4H), 5·68 (2H), 3·69 s (1H). (Found: C, 70·69; H, 8·00. $C_{18}H_{24}O_4$ requires: C, 71·03; H, 7·95%).

1,1-Diphenylethynyl-2,2-dicyanoethene (**22**). Solns of **1a** (0·5 g) in MeOH (5 ml), excess malononitrile in methanol (5 ml) and sat MeONa (3 ml) were mixed, warmed to 40° for 5 min. The mixture was cooled, acidified with AcOH, treated with water and cooled to ca. 0° overnight. A tan solid (0·2 g) was deposited from the purple soln. The yellow solid had m.p. 144·5–146°, from MeOH; ν^{Nujol} 2170 (CN); τ^{DMSO} ~2·4 (aryl). (Found: C, 86·55; H, 3·78). $C_{20}H_{10}N_2$ requires: C, 86·31; H, 3·62%).

3-Phenyl-4-acetyl-4-carbethoxy-5-benzylidenecyclopent-2-eneone (**23**). A soln of MeONa (0·075 g) in MeOH (35 ml) was added to **1a** (2 g, 0·0087 mole) and acetoacetic ester in MeOH (75 ml) at 0°. The reddish soln was kept at 0° for 75 min, then neutralized with glacial AcOH. The solvent was removed under vacuum and the residue was washed with MeOH. After recrystallization from MeOH, the solid **23** (1·35 g or 43% yield) had m.p. 114–116°; ν^{KBr} 3060, 2990, 1748 (COOR), 1710 ($COCH_3$), 1678 (CO), 1612 (C=C); τ^{CDCl_3} 9·08 t (3H, J = 7 c/s), 8·08 s (3H), 5·98 q (2H, J = 7 c/s), 2·93 s (1H), 2·3 s (1H), 2·6 m (aryl). (Found: C, 76·66; H, 5·67. $C_{23}H_{20}O_4$ requires: C, 76·64; H, 5·59%).

3-Phenyl-4-carbethoxy-5-benzilidenecyclopent-2-eneone **24**. This compound is found along with **23**. To prepare it, to **23** (1·5 g, 0·0042 mole) in MeOH soln (125 ml), we added MeONa (0·45 g, 0·0083 mole) in MeOH (50 ml) at 0°. After 165 min, the soln was neutralized with glacial AcOH (ca. 0·6 ml) and worked up to give a light tan solid (0·9 g, 68% yield). This had m.p. 144–147°, from MeOH; ν^{KBr} 2992, 2950, 1725 (COOR), 1680 (CO), 1627 (C=C) cm^{-1}; τ^{CDCl_3} 9·17 t (3H, J = 7 c/s), 6·22 q (2H, J = 7 c/s), 4·97 m (1H), 3·31 d (1H, J = 1·4 c/s), ~2·9 m (11H). (Found: C, 79·01; H, 5·67. $C_{21}H_{18}O_3$ requires: C, 79·22; H, 5·69%).

3-Phenyl-4-carbethoxy-5-benzylcyclopent-2-eneone (**25**). Compound **24** (1·65 g) was reduced with H_2 (20 psi) in ether (250 ml) in the presence of 5% Pd–C (0·5 g). After the press dropped to 13 psi, the reaction was stopped and the product worked up: a crude residue was recrystallized from ether–Skelly B (V/V 3/2). The clean product melted over the range 100–108°, presumably because of isomerization. It had: ν^{KBr} 2980, 2900, 1715 (COOR), 1685 (CO); τ^{CDCl_3} 9·02 t (3H, J = 7 c/s), 6–7·5 m (2 + 2 + 1H), 5·78 two d (1H, J_{cis} ~ 5·5 c/s, $J_{2,4}$ ~ 1 c/s), 3·50 d (=CH, J = 1 c/s), ~2·9 m (aryl). (Found: C, 78·66; H, 6·16. $C_{21}H_{20}O_3$ requires: C, 78·72; H, 6·29%).

REFERENCES

[1] This investigation was supported by Public Health Service Grant GM 7021. Inquiries should be addressed to S.I.M.

[2] National Science Foundation Undergraduate Research Participant, 1964–1966.

[3] I. M. Mathai, H. Taniguchi and S. I. Miller, *J. Am. Chem. Soc.* **89**, 115 (1967); *Tetrahedron* **22**, 867 (1966).

[4] B. W. Nash, D. A. Thomas, W. K. Warburton and T. D. Williams, *J. Chem. Soc.* 2983 (1965).
[5] G. Dupont, *Bull. Soc. Chim. Fr* **41**, 1167 (1927).
[6] K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 45 (1946).
[7] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *Ibid.* 39 (1946).
[8] K. Bowden and E. R. H. Jones, *Ibid.* 953 (1946).
[9] K. Bowden, E. A. Braude and E. R. H. Jones, *Ibid.* 945 (1946).
[10] U. Türck and H. Behringer, *Chem. Ber.* **98**, 3020 (1965); R. Huisgen, R. Knorr, L. Möbius and G. Szeimies, *Ibid.* **98**, 4014 (1965).
[11] C. L. Bickel, *J. Am. Chem. Soc.* **72**, 1022 (1950).
[12] K. Bowden and E. R. H. Jones, *J. Chem. Soc.* 52 (1946).
[13] A. W. Johnson and R. R. Melhuish, *Ibid.* 346 (1947).
[14] C. K. Liang, *Bull. Soc. Chim. Fr* (4)**53**, 33, 41 (1933).
[15] J Chauvelier, *Ann. Chim.* (12)**3**, 393 (1948); *Bull. Soc. Chim. Fr* (5)**21**, 734 (1954) and refs cited herein.
[16] F. Gaudemar-Bardone, *Ann. Chim.* (13)**3**, 52 (1958); *C.R. Acad. Sci., Paris* **238**, 1716 (1954).
[17] F. Wille and R. Strasser, *Chem. Ber.* **94**, 1606 (1961).
[18] T. Böhm-Gössl, W. Hunsman, L. Rohrschneider, W. M. Schneider and W. Zeigenbein, *Chem. Ber.* **96**, 2504 (1963).
[19] G. O. Dudek, *J. Am. Chem. Soc.* **85**, 694 (1963); G. O. Dudek and R. H. Holm, **84**, 2691 (1962); G. O. Dudek, *J. Org. Chem.* **32**, 2017 (1967).
[20] R. S. Atkinson and E. Bullock, *Canad. J. Chem.* **41**, 625 (1963); A. R. Katritzky and J. M. Lagowski, *Adv. in Heterocyclic Chem.* **2**, 1 (1963), and refs herein.
[21] A. Treibs and A. Ohorodnik, *Liebigs Ann.* **611**, 139, 149 (1958); A. Treibs and F. Reitsam, *Ibid.* **611**, 205 (1958).
[22] A. I. Kosak, R. J. F. Palchak, W. A. Steele and C. M. Selwitz, *J. Am. Chem. Soc.* **76**, 4450 (1953); P. Friedlaender and St. Kielbasinski, *Ber. Dtsch. Chem. Ges.* **45**, 3389 (1912).
[23] S. Gronowitz and A. Bugge, *Acta Chem. Scand.* **20**, 261 (1966); H. J. Jakobsen and S.-O. Lawesson, *Tetrahedron* **21**, 3331 (1965); S. Gronowitz, *Adv. in Heterocyclic Chem.* **1**, 82 (1963).
[24] We are grateful to Mr. K. Migliorese for these observations.
[25] [a] W. L. Dilling, *J. Org. Chem.* **31**, 1045 (1966); E. J. Moriconi, W. F. O'Connor and W. F. Forbes, *J. Am. Chem. Soc.* **84**, 3928 (1962);
[b] D. Buza and W. Polaczkowa, *Tetrahedron* **21**, 3409 (1965);
[c] R. F. Rekker and W. T. Nauta, *Rec. Trav. Chim.* **80**, 747, 764 (1961).
[26] G. Stork and M. Tomasz, *J. Am. Chem. Soc.* **86**, 471 (1964).
[27] J. G. Dinwoodie, H. M. White and W. J. Day, *J. Org. Chem.* **27**, 327 (1962).
[28] U. Schmidt and M. Schwochan, *Chem. Ber.* **97**, 1649 (1964).
[29] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.* **80**, 6360 (1958).