Base-induced Rearrangement of γ-Diketones. I. The Rearrangement of 1,2,2-Triphenyl-1,4-pentanedione to 1,3,3-Triphenyl-1,4-pentanedione[1]

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Treatment of 4-hydroxy-2,2-diphenyl-3-pentenoic acid lactone (**3**) with phenyllithium gives 1,2,2-triphenyl-1,4-pentanedione (**2**), 1,3,3-triphenyl-1,4-pentanedione (7), and 3,3-diphenylpropiophenone (**16**). The γ-diketone **7** is shown to arise via rearrangement of an anion of the γ-diketone **2**. The formation of 1,2,3-triphenyl-1,4-pentanedione (27) is not observed, nor is **27** converted to **7** on treatment with base. It is concluded that the rearrangement proceeds via two homoenolate anion intermediates rather than via two 1,2 phenyl shifts.

Le traitement de la lactone de l'acide hydroxy-4 diphényl-2,2 pentène-3 oique (**3**) avec le phényllithium conduit aux triphényl-1,2,2 pentanedione-1,4 (**2**), triphényl-1,3,3 pentanedione-1,4 (**7**), et diphényl-3,3 propiophénone (**16**). Il est montré que la γ-dicétone **7** provient d'une transposition de l'anion de la γ-dicétone **2**. La formation de la triphényl-1,2,3 pentanedione-1,4 (**27**) n'est pas observée; par traitement basique **27** n'est pas non plus transformé en **7**. On en déduit que la transposition procède par l'intermédiaire de deux anions homoénolates plutôt que par deux migrations 1,2 de phényle.

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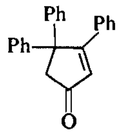
In connection with studies of the i.r. spectra of cyclopentenones (2), the synthesis of 3,4,4-triphenyl-2-cyclopentenone (**1**) was undertaken. It was anticipated that this could be prepared from 1,2,2-triphenyl-1,4-pentanedione (**2**), which could be obtained by the reaction of the lactone **3** with phenyllithium. Previous work (3) suggested that **3** could be prepared by the reaction of diazoacetone (**4**) with diphenylketene (**5**).



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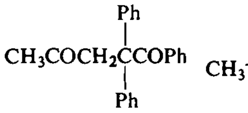
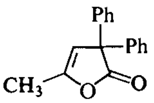


$$CH_3COCH_2\overset{Ph}{\underset{Ph}{C}}COPh$$

2



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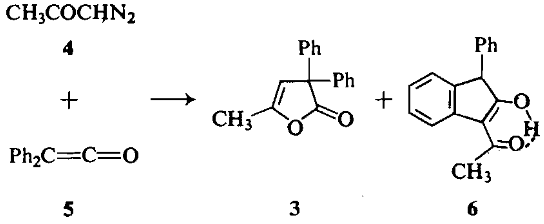
In the event (Scheme 1), the reaction of **4** with **5** gave a mixture of products from which two compounds, $C_{17}H_{14}O_2$, were isolated. One of these, obtained in 11% yield, is identified as the desired lactone **3** by its i.r. and p.m.r. spectra.[2] The other, major product is assigned structure **6** (or the alternative enol) on the basis of its spectra[2] and the fact that it gives a positive test for a chelated enol on treatment with anhydrous methanolic ferric chloride; the formation of this type of product finds analogy in the reaction of diphenylketene with ethyl diazoacetate reported by Kende (4).

When the lactone **3** was treated with phenyllithium in ether for 20 min followed by work-up in aqueous acid, three products were obtained (Scheme 2). Two of these are isomers, $C_{23}H_{20}O_2$, and on the basis of their spectra (Table 1) are considered to be **2** and 1,3,3-triphenyl-1,4-pentanedione (**7**). The relationship of the u.v. spectra of the two isomers led to the assignment of structure **2** to the compound m.p. 154.5–155.5° (42%) and of structure **7** to the compound m.p. 152.5–154° (4%), in that the hypsochromic and hypochromic shifts of the high intensity maximum in the spectrum of the former relative to the latter can be attributed to a departure from coplanarity of the benzoyl phenyl and carbonyl groups of **2** due to the adjacent *gem*-diphenyl grouping. These assignments were corroborated by conversion of



SCHEME 1

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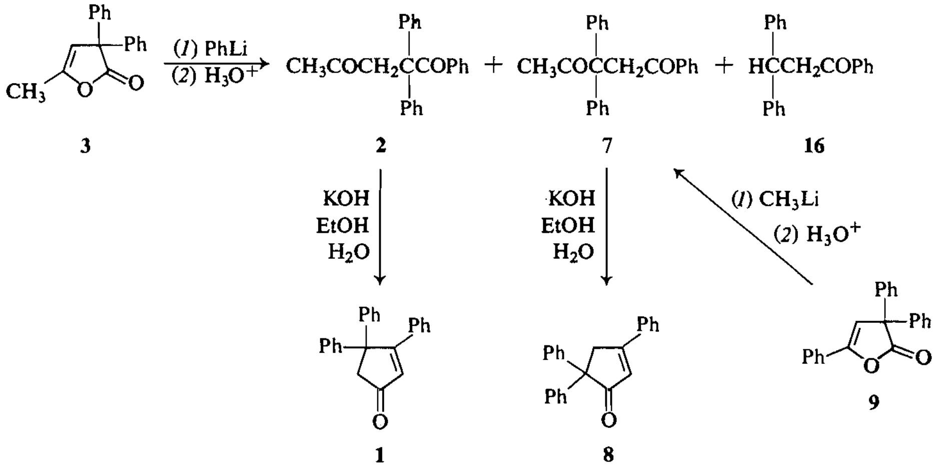
[1] Preliminary reports on part of this work have appeared (1).

[2] See Experimental.

TABLE 1. Spectra of 1,2,2- and 1,3,3-triphenyl-1,4-pentanediones

Compound	2	7
Melting point (°C)	154.5–155.5	152.5–154
λ_{max} (CCl_4) (μ)	5.79, 5.96, 7.36 (m)	5.85 (sh), 5.90, 7.40 (m)
λ_{max} (EtOH) [mμ(ε)]	239 (9800), 316 (sh, 310)	242.5 (13 800), 276.5 (sh, 1580)
δ ($CDCl_3$)	1.91 (s, 3H), 3.71 (s, 2H), 7.0–7.6 (m, 15H)	2.17 (s, 3H), 4.14 (s, 2H), 7.1–7.5 (m, 13H), 7.7–7.9 (m, 2H)



SCHEME 2

2 and 7 with aqueous ethanolic base to the cyclopentenones 1 and 8, respectively. These products are readily distinguishable on the basis of their p.m.r. spectra;[2] as discussed elsewhere (2), the carbonyl-stretching band in the i.r. spectrum of 1 (unsubstituted at C-5) is split while that in the spectrum of 8 (substituted at C-5) is unsplit. Confirmation for the structural assignment for 7 was provided by its independent synthesis by treatment of the lactone 9 with methyllithium. In contrast to 3, 9 was obtained in 77% yield by reaction of diphenylketene (5) with 2-diazoacetophenone (10) (3): two minor products, assigned structures 11 and 12, were also isolated from the reaction mixture (Scheme 3). The i.r. and u.v. spectra of 11 closely resemble those of 13 (5); its formation again finds analogy in the reaction of diphenylketene with ethyl diazoacetate (4). The yellow compound 12 has a u.v. spectrum similar to that of 14 (6) and gives diphenylacetic acid on hydrolysis; its formation can readily be envisaged as proceeding via reaction of 15, the analogue of 6, with diphenylketene.

The third product formed on treatment of lactone 3 with phenyllithium was shown to be 3,3-diphenylpropiophenone (16) by direct comparison with an authentic sample.[3]

The most probable pathway for the formation of the diketone 7 from 3 appeared to be via rearrangement of the anion 17, formed by reaction of 3 with phenyllithium, to the anion 18. That this is the case was indicated by the observation that the yield of 7 relative to 2 increased with longer reaction times. Further, when 2 was treated with sodium methoxide in ether it was converted to a mixture of the cyclopentenones 1 and 8; under these conditions 1 was not converted to 8, and thus it may be concluded that 2 undergoes partial base-induced conversion to an anion of 7, which then gives 8.

Two general types of pathway may be envisaged as accounting for the rearrangement of the anion

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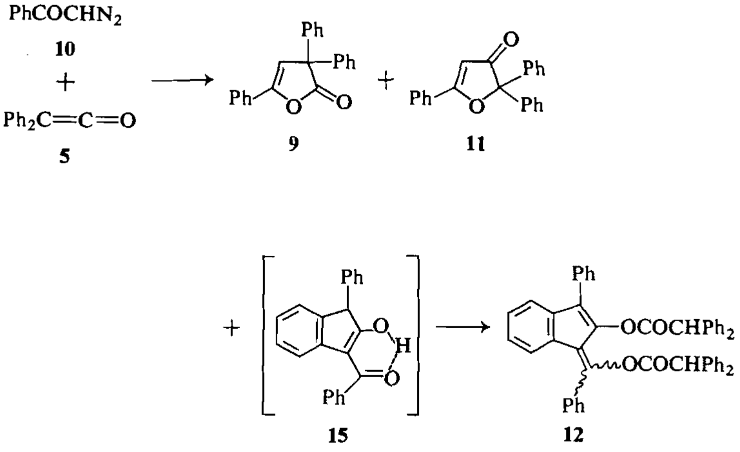
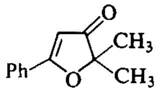
[3] We thank Professor R. E. Lutz, University of Virginia, for his kindness in providing this sample (7).



SCHEME 3



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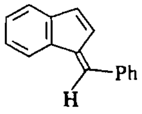

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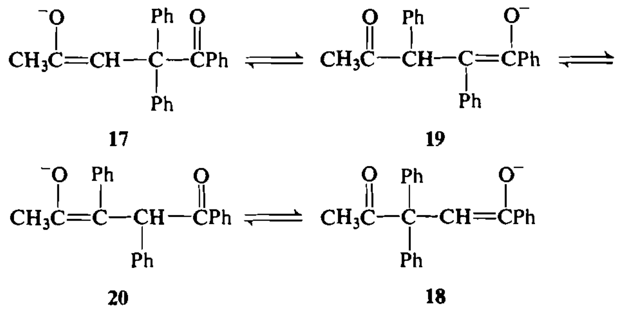

SCHEME 4

17 to the anion **18**.[4] In the first (Scheme 4), migration of a phenyl group could occur to give **19**, followed by hydrogen migration to give **20**, which would give **18** upon migration of the second phenyl group.

Such 1,2 migrations of phenyl groups to anionic centers find ample precedent in the work of Zimmerman, Grovenstein, and their coworkers (8). However, the postulate of a step involving hydrogen migration is less attractive. Consideration of a suprafacial [1,2] sigmatropic shift of hydrogen to an anionic center in terms of conservation of orbital symmetry (9, 10) shows that it is symmetry-forbidden, and no concerted intramolecular pathway is available for such a transformation. The same considerations apply to the more extended π-system of **19**. This restriction does not apply to phenyl migration, where a p-orbital at the migrating carbon atom can be utilized for simultaneous bonding to the atoms between which migration is occurring (9, 11). These considerations do not exclude the possibility that the conversion of **19** to **20** could occur by a non-concerted intramolecular process involving a radical anion – radical pair, as in the case of certain Stevens and Wittig rearrangements (11, 12), or by an intermolecular process involving

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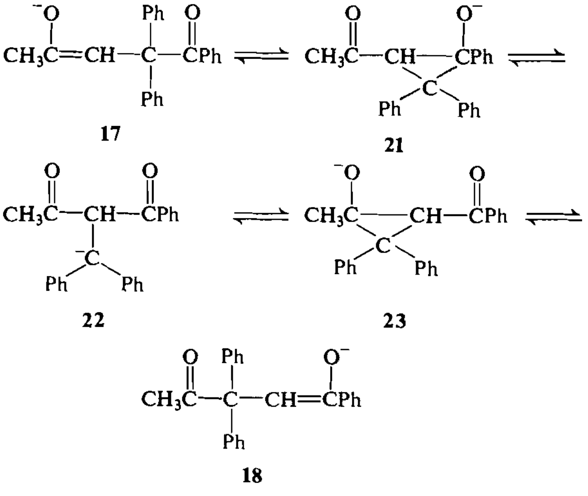
[4] Consideration of the reaction in terms of free anions is, of course, an approximation, since it neglects the presence of the cationoid species. Also neglected are any effects due to the presence of inorganic salts in the organolithium reagents.

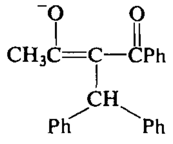
protonation followed by deprotonation. However, the first process seems energetically most unfavorable (12*a*) in the case of hydrogen migration since a hydrogen atom would be one member of the radical pair, while the second process is likely to be unfavorable since it would require abstraction of a proton from an anionic species.[5]

In the second type of mechanism (Scheme 5), the anion **17** could give the homoenolate anion **21**, followed consecutively by formation of the anion **22** and a second homoenolate anion, **23**, which would give rise to the anion **18**. The intermediacy of homoenolate ions in several base-induced reactions of ketones has been demonstrated by Nickon and others (13), and Freeman and Plonka (14) have proposed the intermediacy of a homoenolate ion in a closely related case. A point of importance relating to Scheme 5 concerns the anion **22**; this is expected to be considerably less stable than the ion **22*a*** that would be derived from it by 1,2 hydrogen migration. Indeed, should **22*a***, the enolate ion of the β-diketone **24**, be formed, it would be anticipated that the reaction would terminate at this stage. However, the suprafacial hydrogen migration required to effect the intramolecular conversion of **22** to **22*a*** is symmetry-forbidden as discussed above, and thus formation of **22*a*** would not be expected to occur readily.

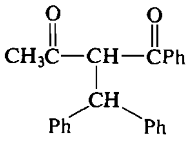
A more concerted version of Scheme 5 is possible and in this connection it is of interest to note its relationship to the mechanism proposed by Woodward and Kovach (15) many years ago for the acid-catalyzed rearrangement of santonic acid (**25**) to parasantonide (**26**). This was postulated to proceed via a concerted process involving (quasi) cyclopropanols analogous to the homoenolate ions **21** and **23**.



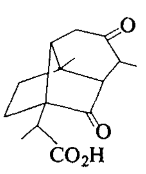
SCHEME 5


$CH_3C(O^-)=C(CH(Ph)_2)-C(=O)Ph$

22*a*


$CH_3C(=O)-CH(CH(Ph)_2)-C(=O)Ph$

24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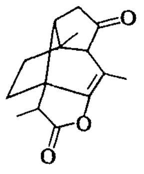
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Scheme 5 is preferred to Scheme 4 because of the inclusion in the latter of a symmetry-forbidden step. Furthermore, experimental evidence confirms that the rearrangement does not proceed via Scheme 4. Were this scheme operative, it would be expected that significant amounts of the anions **19** and **20** would be present in the reaction mixture prior to quenching and that upon quenching the products would include the corresponding protonated species, 1,2,3-triphenyl-1,4-pentanedione (**27**). However, examination of the spectra of the total crude reaction product obtained from the treatment of **3** with phenyllithium failed to reveal the presence of any **27**.

In order to test further the possibility of the intermediacy of **19** and **20** in the rearrangement, the synthesis of the diketone **27** was undertaken. Treatment of deoxybenzoin (**28**) in tetrahydrofuran with sodium hydride followed by 1-bromo-1-phenyl-2-propanone (**29**) gave a mixture of the diastereomers of **27** in low yield (Scheme 6). These were separated by fractional crystallization and identified on the basis of their elemental analyses and spectra (Table 2). Formed in addition were an isomeric compound, considered to

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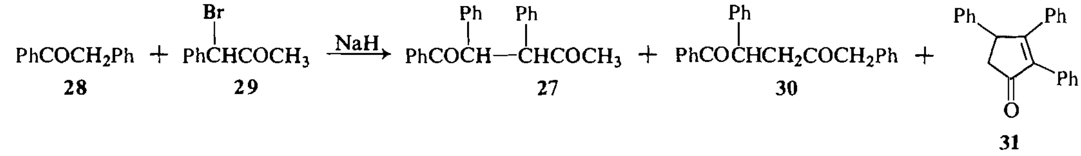
[5] The fact that increase in the reaction time beyond that required for the complete consumption of **3** leads to an increased yield of **7** shows that if an intermolecular proton transfer step is involved it must be able to proceed in the presence of anionic species alone.

TABLE 2. Spectra of the diastereomers of 1,2,3-triphenyl-1,4-pentanedione

Compound	**27***a*	**27***b*
Melting point (°C)	155–155.5	187–188
λ_{max} (CCl_4) (μ)	5.85, 5.96, 7.41 (m), 7.79 (w), 8.02 (w), 14.32	5.85, 5.96, 7.41 (m), 7.83, 14.35
λ_{max} (EtOH) [mμ(ε)]	247 (14 800)	248 (13 200)
δ ($CDCl_3$)	2.15 (s, 3H), 4.60 (d, J = 11 Hz, 1H), 5.20 (d, J = 11 Hz, 1H), 7.3 (m, 13H), 8.05 (m, 2H)	1.92 (s, 3H), 4.84 (d, J = 11 Hz, 1H), 5.60 (d, J = 11 Hz, 1H), 7.4 (m, 13 H), 7.9 (m, 2H)



SCHEME 6

be 1,2,5-triphenyl-1,4-pentanedione (**30**) on spectroscopic grounds,[2] and 2,3,4-triphenyl-2-cyclopentenone (**31**), identified by comparison with an authentic sample (16) (Scheme 6). The relationship between **30** and **31** was confirmed by the observation that the former was converted to the latter by treatment with methanolic sodium methoxide. The pathway for the formation of **30** has not been established; possibilities include (*i*) isomerization of **29** to 1-bromo-3-phenyl-2-propanone followed by reaction with the anion of **28** and (*ii*) isomerization of the enol ether formed by *O*-alkylation of **28** by **29**.

When **27***a*, the lower-melting diastereomer of **27**, was treated with sodium methoxide in ether under conditions that led to the conversion of **2** to a mixture of the cyclopentenones **1** and **8**, neither of these products nor their precursors, **2** and **7**, could be detected in the reaction mixture. Much of compound **27***a* was recovered unchanged, together with several products formed in small amount; one of these was identified as the diastereomer **27***b* on the basis of its R_f value, and another is tentatively considered to be 3,4,5-triphenyl-2-cyclopentenone, the cyclization product from **27**, but was not fully characterized. The fact that **27** is not converted to either **2** or **7** nor to their cyclization products, **1** and **8**, under these conditions excludes it as an intermediate in the conversion of **2** to **7** and thus eliminates a mechanism of the type depicted in Scheme 4.

A mechanism of the type shown in Scheme 5 is therefore considered to be the best representation of the rearrangement pathway. The third product, 3,3-diphenylpropiophenone (**16**), from the reaction of phenyllithium with **3** is formed in variable yield and may result from the adventitious entry of water into the reaction mixture after consumption of the phenyllithium. It might also arise via attack of phenyllithium on **18**, **21**, or **22**. It is not formed by cleavage of **24** during the aqueous work-up, since **24** is stable under these conditions.

Each of the steps in Scheme 5 should be reversible as depicted. However, when the diketone **7** was treated with sodium methoxide in ether, only the cyclopentenone **8** was formed. This suggests that **7** does not undergo significant rearrangement to **2**, although it does not establish this unambiguously since it is possible that cyclization to **8** occurred more rapidly than rearrangement to **2**. Decisive evidence for the failure of the rearrangement to occur in the reverse direction to any significant extent was supplied by the observation that treatment of the lactone **9** with methyllithium gave only **7** and that no trace of **2** could be detected in the p.m.r. spectrum of the crude reaction product after several hours of reaction. It may be concluded that the equilibrium between the anions **17** and **18** very highly favors the latter.[6]

Full acceptance of the type of mechanism shown in Scheme 5 requires the demonstration that the geminal phenyl groups remain attached to the same carbon atom, since this represents a decisive distinction between mechanisms involv-

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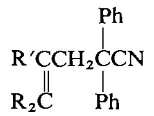
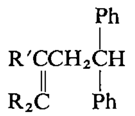
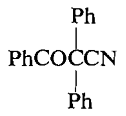
[6] In related cases, it has been established that the rearrangement is reversible; the position of equilibrium in the present case will be discussed in relation to these cases (17).


$\underset{R_2C}{\overset{\|}{R'C}}CH_2\underset{Ph}{\overset{Ph}{C}}CN$

39 R = R′ = Ph
40 R = H; R′ = CH$_3$


$\underset{R_2C}{\overset{\|}{R'C}}CH_2\underset{Ph}{\overset{Ph}{C}}H$

41 R = R′ = Ph
42 R = H; R′ = CH$_3$


$PhCO\underset{Ph}{\overset{Ph}{C}}CN$

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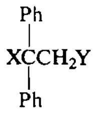
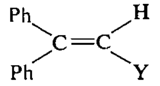
ing homoenolate ions and those involving 1,2 phenyl migrations. In order to test this, methods were sought for the preparation of **2** with an isotopic label at C-3. Its synthesis via **3** was unsatisfactory for this purpose because of the low yield obtained in the preparation of **3**. In spite of a variety of approaches, no success was achieved. Some of the observations made in the course of this search are not without intrinsic interest and they will be discussed here briefly.

Alkylation of diphenylacetonitrile with ethyl bromoacetate in the presence of aqueous sodium hydroxide and benzyltriethylammonium chloride gave the ester **32** in excellent yield.[7] The ester was hydrolyzed to the acid **33**, which was treated with 2 equiv of phenylmagnesium bromide in the expectation that it would be converted to the keto acid **34**. However, elimination of cyanide ion occurred to give the unsaturated acid **35**; a similar result was obtained when phenyllithium was used. When excess Grignard reagent was used the unsaturated alcohol **36** was obtained. The dinitrile **37**, prepared by alkylation of diphenylacetonitrile with chloroacetonitrile (18), on treatment with methylmagnesium iodide or methyllithium gave the unsaturated nitrile **38** in similar fashion.


$X\underset{Ph}{\overset{Ph}{C}}CH_2Y$

32 X = CN; Y = CO$_2$Et
33 X = CN; Y = CO$_2$H
34 X = COPh; Y = CO$_2$H
37 X = Y = CN



35 Y = CO$_2$H
36 Y = CPh$_2$OH
38 Y = CN

Alkylation of diphenylacetonitrile with 2,3,3-triphenylallyl bromide and with methallyl chloride in the presence of 50% aqueous sodium hydroxide and benzyltriethylammonium chloride gave the nitriles **39** and **40**, respectively. It was hoped that treatment of these with methyllithium would convert the nitrile groups to acetyl groups. However, cleavage of a carbon–carbon bond occurred in each case to give the hydrocarbons **41** and **42**, respectively. Such cleavage has been observed in related cases (19) and presumably involves elimination of acetonitrile from the lithium derivative of the imine formed as an intermediate in the attack of the methyllithium on the nitrile group. The preference for elimination in these cases and those referred to above presumably stems from the severe steric crowding at the carbon atom bearing the geminal phenyl groups. A similar cause must underlie the failure of another approach involving attempts to protect the carbonyl group of the keto nitrile **43**, prepared by benzoylation of diphenylacetonitrile.

Although these attempts to find an efficient route for the synthesis of labeled **2** failed, success attended the synthesis of a related labeled γ-diketone, and the study of its rearrangement has corroborated the mechanistic conclusions reached here (*1b*).

Experimental

Reaction of Diazoacetone and Diphenylketene. Formation of 4-Hydroxy-2,2-diphenyl-3-pentenoic Acid Lactone (3) and 3-Acetyl-2-hydroxy-1-phenylindene (6)

A solution of diazoacetone (**4**) was prepared by addition during 2.25 h of acetyl chloride (32.3 g, 412 mmol) in petroleum ether (80 ml) with stirring to 0.704 *M* ethereal diazomethane (1385 ml; 975 mmol) in an ice-water bath. The volume of the solution was reduced to *ca.* 100 ml by evaporation under reduced pressure at room temperature, and the remaining solution was diluted with benzene (800 ml).

This solution was added dropwise to a stirred solution of diphenylketene (**5**)[8] (47.1 g, 242 mmol) in benzene (1 l) at room temperature under nitrogen, and the mixture was stirred under these conditions overnight. The reaction mixture was concentrated to *ca.* 750 ml by distillation under reduced pressure under nitrogen. It was then washed three times with aqueous 5% sodium bicarbonate and once with saturated aqueous sodium chloride, and dried. Removal of the solvent gave a brown oil (57.6 g) from which some **6** (8.49 g) was separated by repeated solution in boiling ether, cooling, scratching, and filtering,

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[7] This method of alkylation, that of Lange and Makosza (18), is preferable to methods involving alkoxides as the basic condensing agent because of its simplicity.

[8] Prepared by the method of Smith and Hoehn (20); to avoid severe bumping and frothing it was found necessary to distil the reaction mixture under nitrogen at water aspirator pressure to remove benzene prior to distillation of the diphenylketene at 3–4 mm.

followed by evaporation of the mother liquor. The residue was dissolved in petroleum ether - benzene (3:2) and chromatographed on silica gel (Davison; 800 g) with the same solvent mixture as eluent; 100-ml fractions were collected. Evaporation of fractions 42–76 gave crude **3** as a yellowish solid (6.05 g). A further quantity of crude **3** was obtained by evaporation of fractions 35–41 and heating of the combined residues at *ca.* 75° (0.025 mm) to volatilize the major contaminant, which was shown to be phenyl benzoate by spectral comparison with an authentic sample.

The total crude **3** (6.87 g) was rechromatographed on silica gel (100 g), packed and eluted with petroleum ether - benzene (3:2); 25-ml fractions were collected. Combination of fractions shown by their i.r. spectra to be rich in **3** and evaporation of the solvent yielded **3** as a colorless solid (6.33 g, 11% based on diphenylketene), m.p. 49–52°; λ_{max} (CCl_4) 5.54, 5.92 μ(m); δ (CCl_4) 2.10 (d, J = 1.5 Hz, 3H), 5.63 (q, J = 1.5 Hz, 1H), 7.26 (s, 10 H). Several sublimations at 70° (0.005 mm) failed to improve the m.p.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.40; H, 5.59.

Further elution of the original chromatographic column with petroleum ether - benzene (3:2) gave **6** which was combined with the material obtained by treatment of the crude reaction product with ether. Eight recrystallizations from hexane gave **6** as colorless crystals, m.p. 125–126°; λ_{max} (CCl_4) 6.03, 6.22 μ(br); λ_{max} (MeOH) 254.5 (ε 9300), 278 (ε 7100), 287.5 (ε 7400), 340 mμ (ε 6000); δ ($CDCl_3$) 2.43 (s, 3H), 4.59 (s, 1H), 7.0–7.5 (m, 9H), *ca.* 14.1 (br s, 1H); blue-green coloration with anhydrous methanolic ferric chloride.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.37; H, 5.69.

Reaction of 3 with Phenyllithium. Formation of 1,2,2-Triphenyl-1,4-pentanedione (2), 1,3,3-Triphenyl-1,4-pentanedione (7), and 3,3-Diphenylpropiophenone (16)

To a solution of **3** (294 mg, 1.18 mmol) in ether (25 ml) was added a 0.291 *M* ethereal solution of phenyllithium (8.0 ml; 2.33 mmol). The mixture was stirred under nitrogen at room temperature for 20 min and then acidified with 1.1 *N* hydrochloric acid. The ethereal phase was washed twice with aqueous 5% sodium bicarbonate and three times with water, and dried. Evaporation of the ether gave an oily solid (400 mg), which was triturated with hexane to give **2** (140 mg). Recrystallization from hexane gave **2** as colorless crystals, m.p. 154.5–155.5°.[9]

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.13; H, 6.34.

The mother liquors were stripped of solvent, and the residue was taken up in chloroform and separated into three major solid fractions by preparative t.l.c. on silica gel plates (with phosphor) with elution with 5% ethyl acetate - carbon tetrachloride. The solid fraction with the lowest R_f value consisted of **2** (55 mg; total yield of pure product: 163 mg, 42%). The next fraction (40 mg) had a closely similar R_f value and was recrystallized from isopropyl alcohol to give **7** (16 mg, 4%) m.p. 146–147°. Three recrystallizations from cyclohexane gave **7** as colorless crystals, m.p. 152.5–154°.[9]

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.99; H, 6.15.

The third solid fraction (28 mg) was recrystallized from methanol to give **16** (19 mg, 6%), m.p. 94–95° (lit. (7) m.p. 94°), undepressed on admixture with an authentic sample;[3] λ_{max} ($CHCl_3$) 5.93 μ; λ_{max} (EtOH) 241.5 mμ (log ε 13 200); δ ($CDCl_3$) 3.68 (d, J = 7.3 Hz, 2H), 4.83 (t, J = 7.3 Hz, 1H), 7.0–7.5 (m, 13H), 7.8–8.0 (m, 2H).

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.13; H, 6.32.

When the reaction time was extended to 2.5 h and the product mixture was again resolved by preparative t.l.c. and crystallization, there was obtained **2** (18%) and **7** (27%) together with the corresponding cyclopentenones **1** (3%) and **8** (5%) (*vide infra*) (total yields of unrearranged and rearranged products: 21 and 32%, respectively).

Reaction of 2 with Aqueous Ethanolic Potassium Hydroxide. Formation of 3,4,4-Triphenyl-2-cyclopentenone (1)

A solution of **2** (248 mg, 0.756 mmol) in a 5% solution of potassium hydroxide in ethanol–water (4:1, 15 ml) was boiled under reflux for 30 min. The mixture was neutralized with 2 *N* hydrochloric acid and diluted with water, and solvent was distilled until the vapor temperature reached 98°. The residue was extracted four times with dichloromethane, and the extracts were washed twice with water and dried. Evaporation of the solvent gave a solid, which was crystallized from ethanol to yield **1** (117 mg, 50%), m.p. 173–179°. Further recrystallization from several solvents did not give a sharp-melting solid; the product consisted of two types of crystals, long needles and irregular globular forms, that were separated by hand picking and shown to have identical i.r. spectra in solution; λ_{max} (CCl_4) 5.80 (sh), 5.87 μ; λ_{max} (EtOH) 290 mμ (ε 17 000); δ ($CDCl_3$) 3.30 (s, 2H), 6.84 (s, 1H), 7.0–7.5 (m, 15H).

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.86; H, 5.83.

Reaction of 7 with Aqueous Ethanolic Potassium Hydroxide. Formation of 3,5,5-Triphenyl-2-cyclopentenone (8)

A solution of **7** (64 mg, 0.20 mmol) in a 5% solution of potassium hydroxide in ethanol–water (4:1) was boiled for 30 min. Work-up as in the case of **2** above gave a solid, which was crystallized from methanol to yield **8** (38 mg, 63%), m.p. 152–154°. This product was also obtained, together with **1**, when a mixture of **2** and 7 was chromatographed on neutral alumina; one recrystallization from hexane and two from methanol gave an analytical sample, m.p. 155–156.5°; λ_{max} (CCl_4) 5.87 μ; λ_{max} (EtOH) 288.5 mμ (ε 22 900); δ ($CDCl_3$) 3.83 (d, J = 1.5 Hz, 2H), 6.63 (t, J = 1.5 Hz, 1H), 7.0–7.9 (m, 15H).

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.77; H, 5.93.

Reaction of 2-Diazoacetophenone and Diphenylketene. Formation of 4-Hydroxy-2,2,4-triphenyl-3-butenoic Acid Lactone (9), 2,2,5-Triphenyl-3(2H)-furanone (11), and 12[10]

To a solution of 2-diazoacetophenone (**10**) (21) (4.25 g, 29 mmol) in ether (30 ml) was added diphenylketene (**5**)

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[9] For spectra, see Table 1.

[10] *Cf.* ref. 3.

(22) (6.25 g, 32 mmol) in a nitrogen atmosphere. Brisk evolution of nitrogen occurred and the mixture was stirred under nitrogen at room temperature for 2 h, and then heated under nitrogen on the steam bath for a further 2 h after removal of most of the ether. The resulting oil (10.75 g) was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on a silica gel column (Davison; 800 g) packed in the same solvent. The column was eluted with petroleum ether containing increasing amounts of ether (2% increments). Elution with 8% ether – petroleum ether gave **9** (7.00 g, 77% based on **10**), which was obtained after recrystallization from ethanol as colorless needles, m.p. 117.5–118.5° (lit. (3) m.p. 121–121.5°, 120°); λ_{max} 5.55, 6.03 μ(w); δ ($CDCl_3$) 6.33 (s, 1H); 7.2–7.5 (m, 13H), 7.6–7.8 (m, 2H).

The fractions eluted with 20% ether–petroleum gave **12** (2.17 g, 11%), which was obtained after recrystallization from ethanol as yellow needles, m.p. 183–184°; λ_{max} 5.71, 6.15 μ(m); λ_{max} (EtOH) 253 (ε 20 100), 259 (ε 19 400), 283.5 (ε 16 700), 333.5 mμ (ε 14 300); δ ($CDCl_3$) 3.90 (s, 1H), 5.34 (s, 1H), 6.8–7.6 (m, 34H).

Anal. Calcd. for $C_{50}H_{36}O_4$: C, 85.70; H, 5.18. Found: C, 85.21, 85.13; H, 5.09, 5.03.

Hydrolysis of **12** in 2-methoxyethanol with aqueous sodium hydroxide on the steam bath followed by recrystallization of the acid fraction from petroleum ether gave diphenylacetic acid, m.p. 146–147°, undepressed on admixture with an authentic sample; the i.r. spectra of the two samples were identical.

The fractions eluted with 26–28% ether – petroleum ether gave **11** (0.76 g, 8%), which was obtained after recrystallization from ethanol as colorless needles, m.p. 175–175.5°; λ_{max} (CCl_4) 5.89 μ; λ_{max} (EtOH) 247 (ε 6100), 309 mμ (ε 16 900); δ ($CDCl_3$) 6.11 (s, 1H), 7.35–7.6 (m, 13H), 8.0 (m, 2H); *m/e* (relative abundance) 312 (43), 283 (16), 207 (98), 179 (100), 105 (47).

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.36; H, 5.25.

Reaction of 9 with Methyllithium. Formation of 7

To a solution of **9** (500 mg, 1.60 mmol) in ether (40 ml) under nitrogen was added 1.75 *M* ethereal methyllithium (1.5 ml, 2.6 mmol). The mixture was stirred at room temperature for 25 min and then treated with 2 *N* sulfuric acid (15 ml). The ethereal layer was separated, washed with aqueous sodium bicarbonate and saturated aqueous sodium chloride, and dried. Evaporation of the ether gave a white solid that was crystallized from methanol to give **7** (470 mg, 89%), m.p. 148–148.5°. The p.m.r. spectrum of the crude product gave no evidence for the presence of **2**. When the reaction was allowed to proceed for 5 h, the yield of **7** was reduced to 77%, but again the p.m.r. spectrum of the crude product failed to show the presence of **2**.

Reaction of 2 with Sodium Methoxide in Ether

Sodium hydride (22 mg of a 54% dispersion in mineral oil; 0.49 mmol) was washed twice with petroleum ether and once with ether to remove mineral oil, and suspended in ether (25 ml) with stirring under nitrogen. To the stirred suspension was added a solution of **2** (127 mg, 0.39 mmol) in ether (35 ml) followed by two drops of methanol. After 3 days the mixture was treated with 1.2 *N* hydrochloric acid (25 ml). The ethereal layer was separated, and the aqueous layer was extracted twice with ether. The combined ethereal solutions were washed with aqueous 5% sodium bicarbonate and dried. The solvent was evaporated to give a solid residue (110 mg), which was resolved into two major components by preparative t.l.c. on silica gel (with phosphor) with elution with 5% ethyl acetate – carbon tetrachloride. The faster-moving major component (32 mg) was recrystallized from hexane–methanol to give **8** as colorless needles (25 mg, 21%), m.p. 150.5–152.5°. The slower-moving major component (43 mg) was crystallized from cyclohexane to give **1** as colorless crystals (35 mg, 29%), m.p. 168–173°.

When a solution of **1** in ether was treated with sodium hydride and methanol for 3 days and the mixture was worked-up as above, **1** was recovered quantitatively.

When a solution of **7** (61 mg) in ether was treated similarly, it was converted to **8** (43 mg, 75%), m.p. 148–150°; the p.m.r. spectrum of the total crude reaction product failed to show the presence of **1**.

Reaction of the Sodium Derivative of Deoxybenzoin with 1-Bromo-1-phenylacetone. Formation of the Diastereomers of 1,2,3-Triphenyl-1,4-pentanedione (27), 1,2,5-Triphenyl-1,4-pentanedione (30), and 2,3,4-Triphenyl-2-cyclopentenone (31)

Sodium hydride (460 mg of 54% dispersion in mineral oil; 10.3 mmol) was suspended in tetrahydrofuran (15 ml) in a nitrogen atmosphere. Deoxybenzoin (1.96, 10.0 mmol) dissolved in a little tetrahydrofuran was added. The mixture was warmed for 15 min, after which time hydrogen evolution had ceased. 1-Bromo-1-phenylacetone (23) (2.13 g, 10 mmol) was added and the mixture was boiled under reflux for 5 h. It was then poured into water and extracted with benzene. The extract was dried and stripped of solvent to give an orange gum, which was chromatographed on silica gel (150 g) packed in benzene–petroleum ether (2:3). Elution was commenced with mixtures of these solvents, the proportion of benzene being progressively increased. With benzene as eluent, deoxybenzoin (1.42 g, 72% recovery) was eluted. Elution was continued with benzene containing increasing amounts of ether. With 10% ether an oil (1.37 g) was eluted that was fractionated by preparative t.l.c. on silica with multiple gradient elution with 2–6% ether in petroleum ether to give a mixture of the diastereomers **27** (259 mg, 8%), together with **30** (409 mg, 12.5%) and **31** (233 mg, 7.5%) as the major components in order of decreasing R_f values.

Crystallization of the mixture of diastereomers **27** from methanol (20 ml) gave **27*b*** as colorless needles (55 mg), m.p. 187–188° after recrystallization from methanol.[11]

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.94; H, 6.11.

On slow evaporation of the mother liquors a mixture of fine needles (**27*b***) and large prisms (**27*a***) crystallized. On dilution with methanol and heating, the needles dissolved more rapidly than the prisms, which were separated by filtration of the hot solution. Recrystallization from methanol gave **27*a***, m.p. 155–155.5°.[11]

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.87, 84.58; H, 6.54, 6.18.

Concentration of the mother liquors followed by

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[11] For spectra, see Table 2.

repetition of the above separation processes together with hand-picking of crystals gave further **27*b*** (total yield: 80 mg), m.p. 187–188°, and **27*a*** (total yield; 137 mg), m.p. 154–155°.

Several recrystallizations of **30** from methanol gave crystals, m.p. 112.5–113°; $\lambda_{\max}$ (CCl_4) 5.86, 5.97 μ; $\lambda_{\max}$ (EtOH) 246 mμ (ε 13 600); δ ($CDCl_3$) 2.76 (dd, *J* = 4, 18 Hz, 1H), 3.62 (dd, *J* = 10, 18 Hz, 1H), 3.74 (s, 2H), 5.13 (dd, *J* = 4, 10 Hz, 1H), 7.26 (m, 13H), 8.0 (m, 2H); *m*/*e* (relative abundance) 328 (0.8), 237 (47), 105 (100).

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.24; H, 6.09.

Compound **31** was purified by preparative t.l.c. on silica with multiple elution with 5% ether – petroleum ether followed by recrystallization from methanol with treatment with Norit. It was obtained as pale yellow prisms, m.p. 139.5–140.5°, undepressed on admixture with an authentic sample prepared by the method of Koelsch and Geissman (16*a*); the i.r. spectra of the two samples were identical.

Reaction of 30 with Aqueous Ethanolic Sodium Hydroxide

A solution of **30** (59 mg) in ethanol (2 ml) was treated with 1 *N* aqueous sodium hydroxide (0.4 ml), and the resulting yellow solution was warmed briefly on the steam bath, acidified by the addition of 1 *N* hydrochloric acid (0.45 ml), and evaporated to dryness. The organic material was extracted from the residue with methanol, and the extract was concentrated to small volume. On standing, the concentrate deposited yellow crystals, which were recrystallized from methanol to give **31** (35 mg, 63%) as very pale yellow prisms, m.p. 140–140.5°, undepressed on admixture with an authentic sample (16*a*).

Reaction of 27a with Sodium Methoxide in Ether

Compound **27*a*** (27 mg, 0.082 mmol) in ether (15 ml) was treated with sodium hydride (7.4 mg of a 54% dispersion in mineral oil; 0.17 mmol) and methanol (one drop) as in the case of **2**. Preparative t.l.c. on silica gel (with phosphor) with multiple elution with 50 and 80% benzene – petroleum ether gave **27*a*** (18 mg, 67%) and several minor fractions, which did not include **1**, **2**, **7**, or **8**. One of these fractions (2.5 mg) had an R_f value identical with that of **27*b***. A second (4 mg) was tentatively identified as 3,4,5-triphenyl-2-cyclopentenone: $\lambda_{\max}$ (CCl_4) 5.85 μ; $\lambda_{\max}$ (EtOH) 286.5 mμ (ε ~ 14 000); δ ($CDCl_3$) 3.53, 4.60, 6.85, 7.3.

2-Benzhydryl-1-phenyl-1,3-butanedione (24)

The β-diketone **24** was prepared from benzhydrol and benzoylacetone by the method of Fosse (24) in 95% yield; m.p. 149.5–150.5° (lit. (24) m.p. 148–150°); $\lambda_{\max}$ 5.78, 5.96 μ; $\lambda_{\max}$ (EtOH) 252 (ε 16 100), 274 mμ (sh, ε 3000); $\lambda_{\max}$ (EtOH–NaOH) 315 mμ (ε 9500); δ ($CDCl_3$) 2.02 (s, 3H), 5.12 (d, *J* = 12 Hz, 1H), 5.63 (d, *J* = 12 Hz, 1H), 7.0–7.5 (m, 13H), 7.9–8.1 (m, 2H).

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.90; H, 6.22.

Compound **24** gave a negative test with anhydrous methanolic ferric chloride and was recovered unchanged after its ethereal solution was stirred for 1 h with either 5% aqueous sodium bicarbonate or 1.2 *N* hydrochloric acid.

Ethyl 3-Cyano-3,3-diphenylpropionate (32)

A mixture of diphenylacetonitrile (1.93 g, 10.0 mmol), 50% aqueous sodium hydroxide (5 ml), and benzene (5 ml) was vigorously stirred to give an emulsion. Benzyltriethylammonium chloride (20 mg) was added, producing an intense red coloration, and the reaction flask was flushed with nitrogen. Ethyl bromoacetate (1.67 g, 10.0 mmol) was added from a dropping funnel. The mixture became warm, and the red color was discharged within 10 min. After 1 h the mixture was poured into water, and extracted with benzene. The extract was washed with dilute hydrochloric acid and saturated aqueous sodium chloride, and dried. Evaporation of the solvent gave a colorless crystalline residue (2.68 g) that was twice recrystallized from ethanol to give **32** (2.10 g, 75%) as colorless prisms, m.p. 103.5–105° (lit. (25) m.p. 103–105°); $\lambda_{\max}$ (CCl_4) 4.49 (w), 5.71, 5.75 μ; δ ($CDCl_3$) 1.10 (t, *J* = 7 Hz, 3H), 3.42 (s, 2H), 4.07 (q, *J* = 7 Hz, 2H), 7.37 (s, 10H).

3-Cyano-3,3-diphenylpropionic Acid (33)

The ester **32** (2.01 g, 7.20 mmol) was dissolved in 70% aqueous ethanol (20 ml) containing potassium hydroxide (4 g), and the solution was heated on the steam bath for 30 min. Acidification with dilute hydrochloric acid gave a copious precipitate, which was filtered and crystallized from aqueous ethanol to give **33** (1.71 g, 95%) as colorless prisms, m.p. 182–183° (lit. (25) m.p. 183–184°); $\lambda_{\max}$ ($CHCl_3$) 3–4, 4.50 (w), 5.79 μ; δ ($CDCl_3$–Me_2CO) 3.48 (s), 7.37 (m), 8.33 (br s).

Reaction of 33 with Phenylmagnesium Bromide or Phenyllithium. Formation of 3,3-Diphenylacrylic Acid (35) and 1,1,3,3-Tetraphenyl-2-propen-1-ol (36)

(*A*) A solution of phenylmagnesium bromide was prepared from magnesium (26 mg, 1.1 mg-at.) and bromobenzene (173 mg, 1.1 mmol) in boiling, dry tetrahydrofuran (5 ml) under nitrogen. The solution was cooled to room temperature, and to it was added a solution of **33** (126 mg, 0.50 mmol) in dry tetrahydrofuran (5 ml). The mixture was stirred overnight, and then treated with 2 *N* sulfuric acid (10 ml). The resulting mixture was boiled under reflux for 45 min, cooled, and extracted with chloroform. The chloroform extract was extracted twice with aqueous 10% sodium carbonate. The combined basic extracts were acidified, and the mixture was extracted with chloroform. This chloroform extract was dried and stripped of solvent to give **35** (95 mg, 85%), which was obtained as long needles, m.p. 160–161° (lit. (26) m.p. 162°) after several crystallizations from aqueous methanol; $\lambda_{\max}$ (CCl_4) 3–4, 5.95 μ; $\lambda_{\max}$ (EtOH) 275 mμ (ε 12 900); *m*/*e* (relative abundance) 224 (100), 207 (18), 179 (42), 178 (37), 123 (13).

(*B*) Compound **33** (500 mg, 1.99 mmol) was treated with phenylmagnesium bromide (23 mmol) in tetrahydrofuran (40 ml) as in section *A*. The mixture was boiled under reflux for 2 h, cooled, and treated with 2 *N* sulfuric acid (25 ml). The resulting mixture was boiled under reflux for 1 h, cooled and extracted with ether. The extract was dried and stripped of solvent to give an orange gum (1.48 g), which was dissolved in 20% benzene – petroleum ether and chromatographed on silica (50 g). Elution was conducted with petroleum ether containing increasing amounts of benzene, followed by benzene. The latter eluted crude **36** (470 mg, 65%), which was crystallized several times from heptane to give prisms, m.p. 137–137.5° (lit. (27) m.p. 138–139°); $\lambda_{\max}$ (CCl_4) 2.80 (m), 6.15 μ (w); δ ($CDCl_3$) 2.44 (s, 1H, absent after D_2O treatment), 6.88 (s, 1H), 7.1–7.6 (m, 20H); *m/e* (relative abundance) 362 (1), 168 (16), 167 (100), 105 (20).

(*C*) A solution of **33** (126 mg, 0.50 mmol) in tetrahydrofuran (6 ml) was treated with a solution of phenyllithium (1.54 mmol) in ether (2 ml). The mixture was boiled under reflux for 5 h and worked-up as in section *A* to give **35** (69 mg, 62%), m.p. 159–160°.

2,2-Diphenylsuccinonitrile (37) (18)

A mixture of diphenylacetonitrile (2.50 g, 13.0 mmol), 50% aqueous sodium hydroxide (10 ml), and benzyltriethylammonium chloride (50 mg) was stirred to give an emulsion. A solution of chloroacetonitrile (0.755 g, 10.0 mmol) in benzene (5 ml) was added at such a rate that the temperature of the mixture was maintained at 30–35° (20 min). After 30 min of stirring, more chloracetonitrile (0.378 g, 5.0 mmol) was added in benzene. After a further 30 min of stirring, the mixture was poured into water. The benzene layer was separated, washed once with water, twice with 2 *N* sulfuric acid, and once with saturated aqueous sodium chloride, dried, and stripped of solvent. The residual solid was twice crystallized from methanol (once with Norit treatment) to give **37** (2.26 g, 75%), m.p. 110–111° (lit. (18) m.p. 111°); λ_{max} ($CHCl_3$) 4.50 μ (m); δ ($CDCl_3$) 3.40 (s, 2H), 7.40 (s, 10H).

Reaction of 37 with Methylmagnesium Iodide or Methyllithium. Formation of 3,3-Diphenylacrylonitrile (38)

A solution of methylmagnesium iodide was prepared from magnesium (27 mg, 1.1 mg-at.) and methyl iodide (156 mg, 1.1 mmol) in ether (3 ml) under nitrogen. To it was added a solution of **37** (116 mg, 0.50 mmol) in ether (15 ml). The mixture was boiled under reflux for 2 h, cooled, and treated with 2 *N* sulfuric acid (5 ml). The resulting mixture was boiled under reflux for 2 h, cooled, and extracted with ether. The extract was washed twice with aqueous 10% sodium carbonate and once with saturated aqueous sodium chloride, dried, and stripped of solvent. The residue was subjected to preparative t.l.c. on silica with five elutions with 25% benzene – petroleum ether. The major fraction was a yellow gum, which on treatment with chloroform gave a small amount of solid residue. Filtration of the chloroform solution and removal of the solvent gave **38** as an oil (54 mg, 53%); λ_{max} (CCl_4) 4.51 μ; δ ($CDCl_3$) 5.73 (s, 1H); 7.3–7.5 (m, 10H).

Similar treatment of **37** (464 mg, 2.00 mmol) in tetrahydrofuran with methyllithium (2.3 mmol) in ether gave **38** as the major product together with unconsumed **37**.

2,2,4,5,5-Pentaphenyl-4-pentenonitrile (39)

A mixture of diphenylacetonitrile (276 mg, 1.43 mmol), 50% aqueous sodium hydroxide (9 ml), and benzene (10 ml) was stirred vigorously under nitrogen to give an emulsion. Benzyltriethylammonium chloride (40 mg) was added to give a deep red coloration, followed by a solution of 2,3,3-triphenylallyl bromide (28) (500 mg, 1.43 mmol) in benzene (20 ml). The red coloration was rapidly lost,[12] and stirring was continued at room temperature for 22 h. The mixture was diluted with an equal volume of water, the benzene layer was separated, and the aqueous layer was extracted twice with benzene. The combined benzene solutions were washed with water and saturated aqueous sodium chloride, dried, and stripped of solvent. The residue was recrystallized from 2-methoxyethanol to give **39** (496 mg, 75%), m.p. 215–217°. Two recrystallizations from this solvent raised the m.p. to 218.5–219°; λ_{max} (CCl_4) 4.49 μ (w); δ ($CDCl_3$) 3.73 (s, 2H), 6.9–7.3 (m, 25H); *m/e* (relative abundance) 461 (1), 270 (28), 269 (100), 193 (19), 192 (14), 191 (43), 178 (8), 165 (15).

Anal. Calcd. for $C_{35}H_{27}N$: C, 91.07; H, 5.90; N, 3.03. Found: C, 91.40; H, 5.82; N, 3.08.

Reaction of 39 with Methyllithium. Formation of 1,1,2,4,4-Pentaphenyl-1-butene (41)

A solution of **39** (335 mg, 0.73 mmol) in dry tetrahydrofuran (25 ml) under nitrogen was treated with 1.75 *M* methyllithium (1.5 ml, 2.6 mmol) in ether. The mixture was stirred at room temperature for 24 h, cooled in ice, and treated with 2 *N* sulfuric acid (6 ml). The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic solutions were washed with aqueous 5% sodium bicarbonate and saturated aqueous sodium chloride, dried, and stripped of solvent to give crystalline **41** (307 mg, 100%), m.p. 152–152.5° after two recrystallizations from heptane; δ 3.22 (d, *J* = 7.5 Hz, 2H), 3.93 (t, *J* = 7.5 Hz, 1H), 6.6–7.4 (m, 25H); *m/e* (relative abundance) 436 (5), 269 (100), 191 (32).

Anal. Calcd. for $C_{34}H_{28}$: C, 93.53; H, 6.47. Found: C, 93.64; H, 6.47.

4-Methyl-2,2-diphenyl-4-pentenonitrile (40)

Diphenylacetonitrile (7.00 g, 36.3 mmol) in benzene (50 ml) was alkylated with methallyl chloride (3.5 g, 39 mmol), 50% aqueous sodium hydroxide (25 ml), and benzyltriethylammonium chloride (200 mg) by the procedure described for the preparation of **39** to give **40** (8.5 g, 95%) as a colorless oil, b.p. 126–127° (0.03 mm); λ_{max} (CCl_4) 4.49 (w), 6.05 μ (m); δ (CCl_4) 1.51 (m, 3H), 3.03 (br s, 2H), 4.69 (m, 1H), 4.86 (m, 1H), 7.3 (m, 10H); *m/e* (relative abundance) 247 (18), 193 (22), 192 (100), 165 (46).

Anal. Calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.46; H, 6.93; N, 5.50.

Reaction of 40 with Methyllithium. Formation of 2-Methyl-4,4-diphenyl-1-butene (42)

A solution of **40** (192 mg, 0.78 mmol) in ether (8 ml) under nitrogen was treated with 1.75 *M* methyllithium (1 ml) in ether. The mixture was stirred for 19 h at −8 to −10°, and then treated with 2 *N* sulfuric acid (5 ml). The resulting mixture was worked-up as in the case of the corresponding reaction of **39** to give **42** as an oil (160 mg, 93%), b.p. 78–80° (0.01 mm); λ_{max} (CCl_4) 6.06 μ (m); δ (CCl_4) 1.63 (m, 3H), 2.71 (d, *J* = 8 Hz, 2H) 4.11 (t, *J* = 8 Hz, 1H), 4.55 (m, 1H), 4.64 (m, 1H), 7.2 (m, 10H).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 92.07; H, 8.10.

3-Oxo-2,2,3-triphenylpropionitrile (43)

Diphenylacetonitrile (965 mg, 5.00 mmol) in benzene (50 ml) was acylated with benzoyl chloride (1.405 g, 10.00 mmol), 50% aqueous sodium hydroxide (25 ml), and benzyltriethylammonium chloride (125 mg) as above, except that the reaction time was reduced to 10 min.

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[12] A run that was terminated at this point showed that the loss of the red color did not signal the completion of the reaction.

Crystallization of the crude product, **43**, from methanol gave colorless prisms (955 mg, 64%), m.p. 125–127°. Recrystallization from methanol raised the m.p. to 128–129°; λ_{max} (CCl_4) 4.48 (w), 5.90 μ; λ_{max} (EtOH) 254.5 mμ (ε 12 500); δ ($CDCl_3$) 7.35 (br s, 13H), 7.8–8.0 (m, 2H); *m/e* (relative abundance) 297 (0.1), 190 (2.5), 165 (13), 106 (8), 105 (100).

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.82; H, 5.09; N, 4.71. Found: C, 85.03; H, 4.99; N, 4.79.

Attempts to ketalize and thioketalize **43** with ethylene glycol and 1,2-ethanedithiol, respectively, were unsuccessful.

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