area associated with these transitions were enhanced by 14 and 5%, respectively. No change was noted in the H-8 transitions. A similar effect was noted when the methine proton in the 1-isobutyryl-4-methoxynaphthalene was irradiated although the NOE was smaller (6 and 2%, respectively). No effect was noted on irradiating the *tert*-butyl methyls of the pivalyl compound. These results are consistent with the earlier data for the aldehyde group. For acetyl, III is still preferred, but as the substituent on the carbonyl groups grows larger in size a nonplanar relation develops between the carbonyl group and the ring. No evidence has been found to suggest that conformation IV is of importance in these substances.

Acknowledgment. This work was supported by the Robert A. Welch Foundation. We wish to express our gratitude to the foundation. One of us (A. M. I.) wishes to express his appreciation to the T. C. U. Research Foundation for a postdoctoral fellowship.

Base-Induced Rearrangement of γ-Diketones. II. Demonstration of the Occurrence of Skeletal Rearrangement and of the Reversibility of the Reaction[1,2]

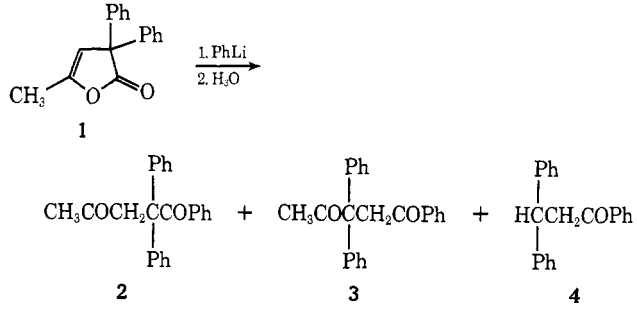
Peter Yates* and Michael J. Betts

Contribution from the Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada. *Received August 23, 1971*

Abstract: 5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione-2-^{13}C, prepared by the reaction of 2-diazoacetophenone-2-^{13}C with diphenylketene to give 4-hydroxy-2,2,4-triphenyl-3-butenoic-3-^{13}C acid lactone followed by treatment of the lactone with *tert*-butyllithium, gave 5,5-dimethyl-1,2,2-triphenyl-1,4-hexanedione-3-^{13}C on treatment in ether with sodium methoxide. The occurrence of skeletal rearrangement is thus demonstrated, and it is concluded that the base-induced interconversion of γ-diketones involves the intermediacy of homoenolate ions rather than 1,2 phenyl migrations. The rearrangement reaction has been shown to be reversible in the cases of 1-(1-naphthyl)-2,2,4-triphenyl-1,4-butanedione and 2,2,4-triphenyl-1-(*p*-tolyl)-1,4-butanedione.

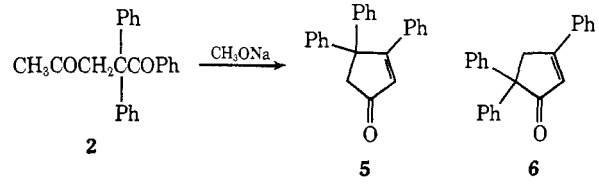
It has recently been reported from these laboratories[1] that treatment of the lactone **1** with phenyllithium followed by aqueous work-up gives 1,2,2-triphenyl-1,4-pentanedione (**2**), 1,3,3-triphenyl-1,4-pentanedione (**3**), and 3,3-diphenylpropiophenone (**4**) (Scheme I). It was concluded that the formation of

Scheme I



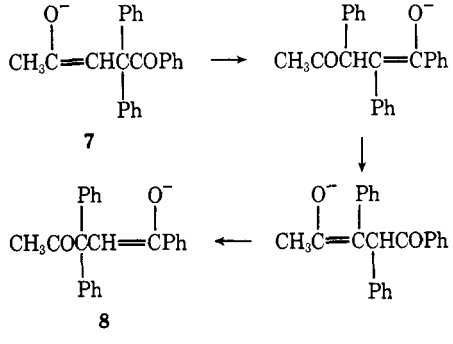
the γ-diketone **3** involved the rearrangement of an enolate ion of the γ-diketone **2** since the yield of **3** relative to **2** increased with longer reaction time. This conclusion was confirmed by the observation that treatment of **2** with sodium methoxide in ether gave a mixture of the cyclopentenones **5** and **6** (Scheme II); under these conditions the cyclopentenones themselves are not interconverted, and thus **2** must have undergone partial base-induced conversion to **3**, which then gave **6**.

Scheme II



Two general types of pathway were considered in accounting for the rearrangement. In one (Scheme III),

Scheme III



the anion **7** derived from **2** is converted to the anion **8** corresponding to **3** by two 1,2 migrations of the phenyl groups with an intermediate 1,2 migration of hydrogen. In the other (Scheme IV), the anion **7** is converted to the anion **8** *via* two homoenolate ions. On both theoretical and experimental grounds the mechanism depicted in

(1) Paper I: P. Yates, G. D. Abrams, M. J. Betts, and S. Goldstein, *Can. J. Chem.*, **49**, 2850 (1971).

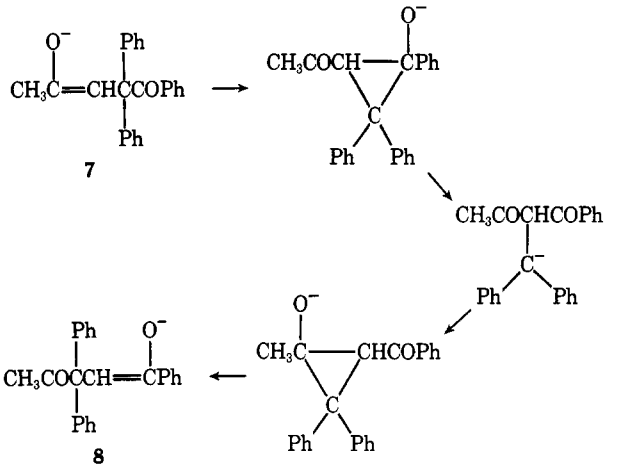
(2) A preliminary report on part of this work has appeared: M. J. Betts and P. Yates, *J. Amer. Chem. Soc.*, **92**, 6982 (1970).

Table I. Spectra of 5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione (**10**), 5,5-Dimethyl-1,2,2-triphenyl-1,4-hexanedione (**11**), 1,3,3-Triphenyl-1,4-pentanedione (**3**), and 1,2,2-Triphenyl-1,4-pentanedione (**2**)

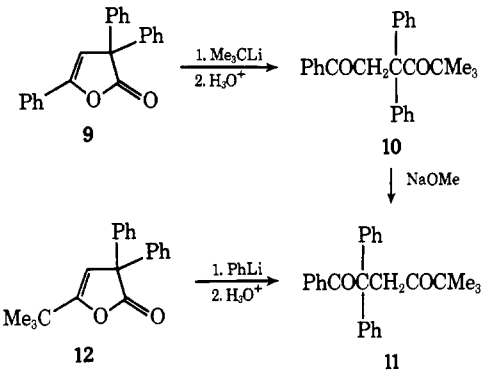
	10	**11**	**3**[a]	**2**[a]
$\lambda_{max}^{CCl_4}$, μ	5.93 (br)	5.85 5.92	5.85 (sh) 5.90	5.79 5.96
λ_{max}^{EtOH}, mμ (ϵ)	244.5 (14,900) 280 (1480)	235 (sh, 9500) 310 (sh, 360)	242.5 (13,800) 276.5 (1580)	239 (9800) 316 (310)
δ^{CDCl_3}	1.01 (s, 9 H) 4.18 (s, 2 H) 7.2–7.6 (m, 13 H) 7.75–7.9 (m, 2 H)	0.85 (s, 9 H) 3.81 (s, 2 H) 7.1–7.6 (m, 15 H)	2.17 (s, 3 H) 4.14 (s, 2 H) 7.1–7.6 (m, 13 H) 7.7–7.9 (m, 2 H)	1.91 (s, 3 H) 3.71 (s, 2 H) 7.0–7.6 (m, 15 H)
m/e (%)[b]	285 (40) 105(100) 85 (8)	265 (8) 105 (38) 85 (33)	285 (9) 105 (100) 43 (3)	223 (9) 105 (74) 43 (100)

[a] Reference 1. [b] Peaks related to Scheme VI.

Scheme IV



Scheme V



Scheme IV (or a more concerted version of it) was favored over that of Scheme III.[1]

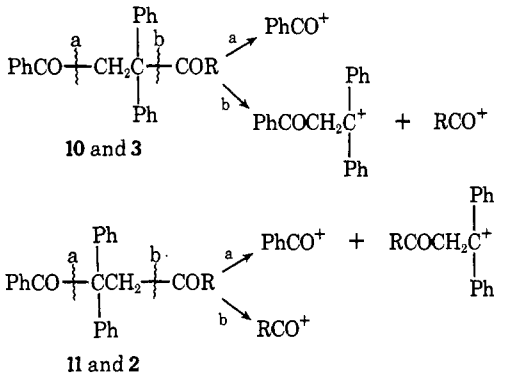
A critical difference between the two types of mechanism is that no skeletal rearrangement occurs in the route involving 1,2 phenyl migrations, while the route involving homoenolate ion formation proceeds with rearrangement of the carbon chain; *i.e.*, C-2 of **2** becomes C-3 of **3**. This difference provides the opportunity to distinguish decisively between the two types of mechanism by the use of carbon isotope labeling. Because of the inefficiency of the synthetic route to **2**,[1] the analogous rearrangement of another γ-diketone, 5,5-dimethyl-1,3,3-triphenyl-1,4-hexanedione (**10**), was chosen for the labeling experiment. This had the additional advantage that the rearrangement reaction would not be accompanied by cyclopentenone formation. The γ-diketone **10** was prepared in 80% yield by treatment of the lactone **9**[1,3] with *tert*-butyllithium in ether at $-10°$ for 2 min followed by work-up with aqueous acid (Scheme V). The assignment of structure **10** to the product is based on its spectra and the relationship of these to the spectra of its rearrangement product, **11** (*vide infra*), and of the γ-diketones **2** and **3** (Table I). Thus, the hypsochromic and hypochromic shifts of the high-intensity maximum in the ultraviolet spectrum of **11** relative to that in the spectrum of **10** are in accord with the presence of the $PhCOCPh_2$ group in the latter but not in the former (*cf.* **2** *vs.* **3**). The relationship between the pmr spectra of **10** and **11** is also closely analogous to that between the pmr spectra of **3** and **2**. The infrared spectrum of **10** is at first sight anomalous in that it shows a single, albeit broad, band in the carbonyl-stretching region at 5.93 μ. However, this can be interpreted in terms of the overlap of the benzoyl carbonyl band with the aliphatic ketone band, which has been shifted to abnormally long wavelength due to angle splaying resulting from complete substitution at both α carbon atoms (*cf.* hexamethylacetone: $\lambda_{max}^{CCl_4}$ 5.93 μ).[4] The mass spectra of **10** and **11** are also related in the same way as those of **3** and **2** in that fragmentation of the molecular ions by fission of the CO–CH_2 bond gives only one ionic fragment, that bearing the positive charge on the carbonyl group, whereas fragmentation of the molecular ion by fission of the CO–CPh_2 bond occurs in both senses to give ions bearing the positive charge on both the carbonyl group and on the CPh_2 carbon atom (Scheme VI). This dichotomy of behavior is clearly attributable to stabilization of the positive charge by the *gem*-phenyl groups.

When a solution of **10** in ether was stirred with sodium methoxide for several days it was converted to the isomeric γ-diketone **11** (Scheme V); after 1 week the conversion was essentially complete (>95%). The structural assignment **11** is based on the spectroscopic relationships (Table I) discussed above and the independent synthesis of the rearrangement product from

(3) P. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961); W. Ried and H. Mengler, *Justus Liebigs Ann. Chem.*, **651**, 54 (1962).

(4) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, 77, 2806 (1955).

Scheme VI



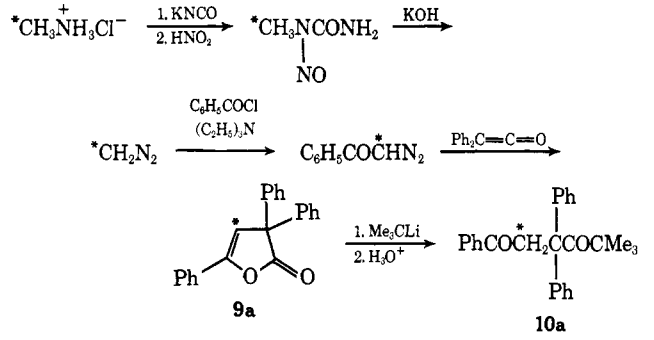
10 and 3

11 and 2

the known lactone **12**[5] by its treatment with phenyllithium followed by work-up with aqueous acid (Scheme V).

2-Diazoacetophenone-*2*-^{13}C was prepared by the route shown in Scheme VII from methylamine-^{13}C hydrochloride (29% enriched) by standard procedures[6,7] that were slightly modified because of the unusually small scale of the operations. It was treated with diphenylketene[1,3] to give the ^{13}C-labeled lactone **9a** which was converted to 5,5-dimethyl-1,3,3-triphenyl-1,4-hexanedione-*2*-^{13}C (**10a**) as before (Scheme VII).

Scheme VII



9a

10a

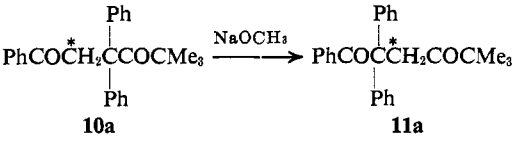
The ^{13}C enrichment at the carbon atoms designated with an asterisk in Scheme VII was determined by measurement of the ^{13}C satellites associated with the pmr signals of the protons on these carbon atoms. The relevant data are given in Table II; in the cases of 2-diazoacetophenone-*2*-^{13}C and **9a** only the upfield ^{13}C satellite signal could be distinguished from other signals; however, in the case of **10a** it was possible to observe both the upfield and downfield ^{13}C satellite signals.

Table II. Measurement of ^{13}C Enrichment in Labeled Compounds by Pmr Spectroscopy

Compd	Solvent	δ	$J_{^{13}C-H}$, Hz	% ^{13}C
$CH_3NH_3^+Cl^-$	D_2O	2.55	144	29 ± 1
$C_6H_5COCHN_2$	CCl_4	5.82	196	27 ± 1
9a	$CDCl_3$	6.33	182	27 ± 1
10a	$CDCl_3$	4.18	129	28 ± 1
11a	$CDCl_3$	3.81	129	28 ± 1

(5) F. R. Japp and W. Maitland, *J. Chem. Soc.*, **85**, 1496 (1904).
(6) F. Arndt, *Org. Syn.*, **15**, 48 (1935); W. E. Bachmann and W. S. Struve, *Org. React.*, **1**, 50 (1942).
(7) P. Yates and B. L. Shapiro, *J. Amer. Chem. Soc.*, **81**, 212 (1959).

Rearrangement of **10a** in ether with sodium methoxide as in the case of **10**, gave **11a**. The position of the labeled carbon was unambiguously established by the pmr spectrum of the product (see Table II), in which both the upfield and downfield ^{13}C satellites could be observed.

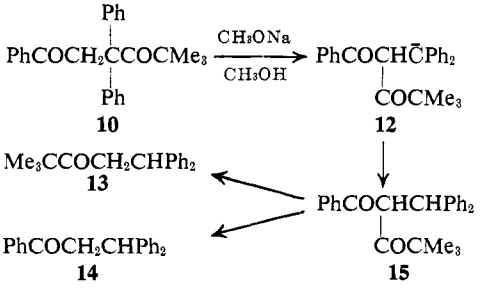


10a 11a

This result, which establishes that the rearrangement reaction is accompanied by skeletal rearrangement, clearly excludes a mechanism of the type shown in Scheme III, and appears only to be interpretable in terms of a mechanism of the type shown in Scheme IV.

As noted earlier, a more concerted version of Scheme IV might be operative. In particular, the interconversion of the homoenolate ions might occur in concerted fashion rather than *via* an intermediate in which a negative charge on carbon is stabilized only by two phenyl groups. Some indication has been obtained, however, that the rearrangement of **10** does in fact proceed *via* the intermediate **12**. Treatment of **10** with methanolic sodium methoxide gave the ketones **13** and **14** in 83 and 5% yield, respectively. The formation of these products can most readily be explained in terms of the formation of **12**, which in the protic medium is protonated to give **15** which in turn undergoes methanolysis to give **13** and **14** (Scheme VIII).[8]

Scheme VIII



10 12 13 14 15

The mechanism that has been proposed for the rearrangement of **2** and **10** to **3** and **11**, respectively, implies that the rearrangement reaction should be reversible. Yet treatment of **3** or **11** in ether with sodium methoxide did not lead to rearrangement. If the rearrangement reaction is reversible, the failure of **3** and **11** to undergo rearrangement requires that the equilibria involved greatly favor these isomers. In order to establish that the rearrangement is in fact reversible, two further cases were examined in which both isomers were expected to be present in significant amount at equilibrium (Scheme IX).

Treatment of the lactone **9** with α-naphthyllithium gave the γ-diketone **16** from which was formed the rearranged γ-diketone **17** on treatment with sodium methoxide. The structural assignments are based on the spectra of **16** and **17** (Table III) and their relationship to those of **2**, **3**, **10**, and **11** (Table I). Separate samples of **16** and **17** were equilibrated in ether with

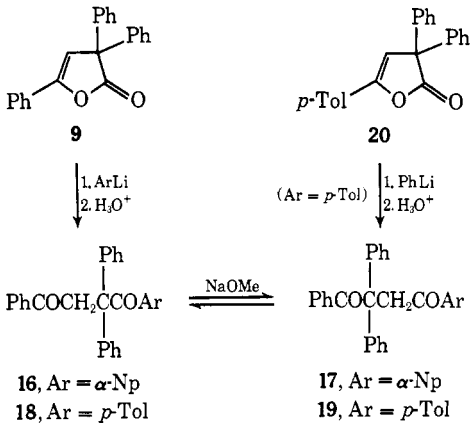
(8) It is also possible that **13** and **14** arise by hydrolytic cleavage of **15** during work-up; however, it has previously been found that the related β-diketone, 2-benzhydryl-1-phenyl-1,3-butanedione, is not cleaved under the work-up conditions.[1]

Table III. Spectra of 1-(1-Naphthyl)-2,2,4-triphenyl-1,4-butanedione (**16**), 4-(1-Naphthyl)-1,2,2-triphenyl-1,4-butanedione (**17**), 2,2,4-Triphenyl-1-(*p*-tolyl)-1,4-butanedione (**18**), and 1,2,2-Triphenyl-4-(*p*-tolyl)-1,4-butanedione (**19**)

	16	**17**	**18**	**19**
$\lambda_{max}^{CCl_4}$, μ	5.93	5.93 (br)	5.89 5.96	5.90 5.95 (sh)
λ_{max}^{EtOH}, mμ (ϵ)	240 (29,300) 294 (6900)	235 (sh, 23,100) 300 (6300)	247.5 (23,300) 310 (sh, 540)	253 (23,100) 310 (sh, 440)
δ^{CDCl_3}	4.41 (s, 2 H) 7.0–7.9 (m, 21 H) 8.45–8.6 (m, 1 H)	4.37 (s, 2 H) 7.1–7.7 (m, 20 H) 7.7–7.8 (m, 2 H)	2.21 (s, 3 H) 4.31 (s, 2 H) 6.99 (d, J = 9 Hz, 2 H) 7.1–7.6 (m, 15 H) 7.85 (dd, J = 8, 2 Hz, 2 H)	2.32 (s, 3 H) 4.30 (s, 2 H) 7.1–7.6 (m, 17 H) 7.76 (d, J = 8.5 Hz, 2 H)
m/e (%)[a]	285 (0.9) 155 (100) 105 (34)	335 (0.7) 155 (100) 105 (51)	285 (1.1) 119 (100) 105 (56)	299 (0.8) 119 (100) 105 (33)

[a] Peaks related to Scheme VI.

Scheme IX



sodium methoxide for 4 days; analysis of the product mixtures by pmr spectroscopy showed that **16** and **17** were converted to mixtures of the two isomers containing 23 and 17% of **16**, respectively. Thus the reversibility of the rearrangement reaction was established and the equilibrium mixture of **16** and **17** shown to be *ca.* 1:4. Similar equilibration experiments were carried out with the γ-diketones **18** and **19** (Table III), prepared by the reaction of the lactone **9** with *p*-tolyllithium and of the lactone **20** with phenyllithium, respectively. After 5 days each isomer gave a mixture of **18** and **19** in the ratio 5:8.[9] The demonstration that the rearrangement reaction is reversible in these cases lends credence to the proposal that the failure to observe rearrangement in the cases of **3** and **11** is due to the fact that they are highly favored over **2** and **10**, respectively, at equilibrium—a circumstance that can be attributed to steric factors.

Experimental Section

Melting points are uncorrected unless otherwise specified. Solutions in organic solvents were dried over anhydrous magnesium sulfate. Petroleum ether refers to a fraction bp 60–70°. Spectra for compounds **10**, **11**, and **16–19** are given in Tables I and III.

(9) In this case, unlike that of **16** and **17**, the mixture was not resolved; identification of the components was based on spectral comparison with **18** and **19**.

5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione (10). A 50-ml three-necked round-bottomed flask was fitted with a condenser, magnetic stirrer, and serum cap. The flask was well flushed with dry nitrogen, and subsequently a static atmosphere of nitrogen was maintained in the flask. The lactone **9**[1] (511 mg, 1.64 mmol) was introduced into the flask followed by ether (20 ml) that had been freshly distilled from sodium. The resulting solution was cooled in an ice–salt bath to −10°. A 2.26 *M* solution of *tert*-butyllithium in pentane (Alfa; 0.80 ml, 1.8 mmol) was added through the serum cap from a syringe, and the mixture was stirred for 2 min and then quenched with 3 *N* hydrochloric acid (6 ml). The ethereal layer was separated, washed consecutively with aqueous sodium bicarbonate and saturated aqueous sodium chloride, and dried. Removal of the solvent and crystallization of the residue (588 mg) from methanol gave **10** as fine needles (486 mg, 80%), mp 130.5–131°; a second crop of crystals (38 mg), mp 129–130.5°, brought the combined yield to 87%. Recrystallization from methanol gave an analytical sample, mp 131–131.5° cor.

Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.20; H, 7.13.

Reaction of 10 with Sodium Methoxide. Formation of 5,5-Dimethyl-1,2,2-triphenyl-1,4-hexanedione (11). In a flask fitted as above were placed **10** (110 mg, 0.30 mmol) and anhydrous ether (15 ml). To the stirred solution were added sodium hydride (49.4 mg of a 53.8% dispersion in paraffin; 1.1 mmol) and 5 drops of methanol, and the mixture was stirred at room temperature for 7 days. It was then quenched with 3 *N* hydrochloric acid (4 ml) and worked up as above. The crude, gummy product (124.5 mg) was dissolved in petroleum ether and chromatographed on a silica column (20 g) made up in the same solvent. Elution with petroleum ether removed the paraffin from the original sodium hydride dispersion. Subsequent elution with 20% ether in petroleum ether gave the product (94.5 mg), which was crystallized from methanol yielding **11** (51 mg, 46%), mp 128–129.5°; a second crop of crystals (18 mg), mp 127–129°, brought the yield to 63%. Recrystallization from methanol gave an analytical sample, mp 130.5–131° cor.

Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.06; H, 7.13.

A thin layer chromatogram and pmr spectrum of the crude reaction product showed it to consist of **11** with a trace, at most, of **10**.

Preparation of 11 from 4-Hydroxy-5,5-dimethyl-2,2-diphenyl-3-hexenoic Acid Lactone (12). The lactone **12** was prepared by the method of Japp and Maitland.[5] Benzil and pinacolone were condensed to give 5,5-dimethyl-1,2-diphenyl-2-hexene-1,4-dione, mp 112.5–114° (lit.[5] mp 115°), which was pyrolyzed at 310° (vapor of boiling diphenylamine) to give a mixture of **12** and the isomeric 2-(*tert*-butyl)-4-hydroxy-3,4-diphenyl-2-butenoic acid lactone in a ratio of 45:55. These were separated by chromatography on silica packed in petroleum ether; elution with 6% ether in petroleum ether gave the lactone **12**, while the isomeric lactone was eluted with 10% ether in petroleum ether. Lactone **12** was recrystallized from ethanol to give colorless needles: mp 152–152.5° (lit.[5]

mp 150°); $\lambda_{max}^{CCl_4}$ 5.57, 6.00 μ (m); δ^{CCl_4} 1.27 (s, 9 H), 5.50 (s, 1 H), 7.23 (s, 10 H).

In a flask fitted as for the preparation of **10** were placed lactone **12** (647 mg, 2.22 mmol) and anhydrous ether (30 ml). A 1.9 *M* solution of phenyllithium in benzene–ether (70:30) (Alfa; 1.33 ml, 2.53 mmol) was added by syringe. The mixture was stirred at room temperature for 15 min and then quenched with 3 *N* hydrochloric acid (10 ml). The ethereal layer was separated, washed successively with 1 *N* aqueous sodium hydroxide, water, and saturated aqueous NaCl, and dried. Removal of the solvent gave a residue that was dissolved in petroleum ether and chromatographed on silica (80 g) packed in the same solvent. Elution with 5% ether in petroleum ether removed biphenyl. Elution with 10% ether in petroleum ether gave essentially pure **11** (769 mg, 94%); a single recrystallization from methanol gave material (619 mg, 75%), mp 128–129°. The spectra of this product were identical with those of the product obtained by treatment of **10** with sodium methoxide; a mixture melting point of the two samples was undepressed.

5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione-2-^{13}C (10a). Methylamine-^{13}C hydrochloride (Merck Sharp and Dohme, Canada, Ltd; 59 ± 1% ^{13}C (see Table II); 250 mg, 3.70 mmol), unlabeled methylamine hydrochloride (250 mg, 3.70 mmol), and potassium cyanate (750 mg, 9.26 mmol) were dissolved in water (2 ml). The solution was boiled under reflux for 25 min and cooled, and sodium nitrite (500 mg, 7.25 mmol) was added. The resulting solution was cooled to 0° and added during 20 min with magnetic stirring to a solution of concentrated sulfuric acid (0.5 ml) in water (3 ml) cooled to −10° in an ice–salt bath. The precipitate was filtered and dried in a desiccator to give 1-methyl-^{13}C-1-nitrosourea (598 mg). The aqueous solution was extracted three times with dichloromethane, and the extract was washed with saturated aqueous sodium chloride, and dried. Removal of the solvent gave further product (32 mg; total yield 85%).

1-Methyl-^{13}C-1-nitrosourea (615 mg, 5.97 mmol) was added slowly with magnetic stirring to a mixture of ether (10 ml) and 50% aqueous potassium hydroxide (5 ml) cooled to −10° in an ice–salt bath. Stirring was continued for 2 hr at −5°. The ethereal solution of diazomethane-^{13}C was decanted onto potassium hydroxide pellets, precooled to −5°; the aqueous solution was washed with four 2.5-ml portions of ether and the washings were added to the original ethereal layer. After 10 min of drying the ethereal solution was decanted from the potassium hydroxide pellets into a precooled 50-ml flask containing a stirring bar. The flask was placed in an ice–salt bath, and to the stirred solution was added anhydrous triethylamine (420 mg, 4.16 mmol). A solution of benzoyl chloride (567 mg, 4.04 mmol) in ether (2 ml) was then slowly added dropwise while stirring was continued and the temperature of the reaction mixture was maintained at −5°. The mixture was stirred for a further 4 hr while the temperature was maintained below 0°. It was then filtered, and the filtrate was evaporated to dryness to give crude 2-diazoacetophenone-2-^{13}C (572 mg). This was crystallized from hexane at −20° to give the product (356 mg, 60% based on benzoyl chloride), mp 46–48° (*cf.* 2-diazoacetophenone, lit.[7] mp 47–48°); a second crop (85 mg), mp 41.5–44.5°, increased the yield to 75%.

In a flask fitted as for the preparation of **10** was placed 2-diazoacetophenone-2-^{13}C (415 mg, 2.84 mmol). Nitrogen was passed through the flask for 30 min, and then anhydrous ether (5 ml) was added from a syringe through the serum cap. To the resulting solution was added in the same fashion diphenylketene[10] (600 mg, 3.09 mmol; weighed under nitrogen), washed in with a little ether. The mixture was stirred for 3 hr at room temperature. The ether was evaporated in a stream of nitrogen, and the residue was heated on a steam bath for 2 hr. The product mixture was added with a considerable volume of boiling petroleum ether to a silica column (100 g) packed in this solvent. Hot, followed by cold, petroleum ether was passed through the column until all the product was adsorbed on the column and the latter had cooled to room temperature. Elution was conducted with petroleum ether containing increasing amounts of ether. Only traces of material were eluted with 2–4% ether. With 6–8% ether 4-hydroxy-2,2,4-triphenyl-3-butenoic-3-^{13}C acid lactone (**9a**) (690 mg, 78%) was eluted. Recrystallization from methanol gave **9a** as colorless crystals (540 mg, 61%), mp 117–117.5° (*cf.* **9**, mp 117.5–118.5°).

5,5-Dimethyl-1,3,3-triphenyl-1,4-hexanedione-2-^{13}C (**10a**) was prepared from **9a** (254 mg, 0.81 mmol) in ether (15 ml) and 2.26 *M* *tert*-butyllithium in pentane (Alfa; 0.40 ml, 0.90 mmol) at −15° as in the case of **10**. The crude product (218 mg) was crystallized from methanol to give **10a** as needles (218 mg, 73%), mp 130–130.5°. The residue from the mother liquors was subjected to preparative thin layer chromatography on a silica plate (20 × 20 × 0.125 cm) with ten elutions with 5–6% ether in petroleum ether; the chromatogram showed a very complex pattern, but the largest, and only, crystalline fraction (22 mg) on recrystallization from methanol gave more **10a** as needles (15.5 mg, total yield 78%), mp 129–130°.

Reaction of 10a with Sodium Methoxide. Formation of 5,5-Dimethyl-1,2,2-triphenyl-1,4-hexanedione-3-^{13}C (11a). Compound **10a** (126 mg, 0.34 mmol) in ether (15 ml) was treated with sodium hydride (51 mg of a 53.8% dispersion in mineral oil; 1.14 mmol) and 3 drops of methanol for 8 days, and the crude product was chromatographed on silica as in the case of **10**. In the present case, however, the material eluted with 20% ether in petroleum ether was a mixture of the rearranged ketone **11a** and the unrearranged ketone **10a** (*ca.* 7:1).[11] The mixture was separated by preparative thin layer chromatography on two silica plates (20 × 20 × 0.125 cm) with eight elutions with 5% ether in petroleum ether. The major component (81 mg) was crystallized from methanol to give **11a** (60 mg, 48%) as colorless needles, mp 128–129°; recrystallization raised the mp to 128.5–129°.

Reaction of 10 with Methanolic Sodium Methoxide. Formation of 5,5-Dimethyl-1,1-diphenyl-3-hexanone (13) and 3,3-Diphenylpropiophenone (14). Compound **10** (243 mg, 0.66 mmol) was added to methanolic sodium methoxide prepared by the addition of sodium (150 mg, 6.5 mg-atoms) to methanol (15 ml), and the mixture was boiled under reflux for 96 hr, when thin layer chromatography indicated that no **10** remained. The mixture was diluted with water and extracted several times with ether. The extract was washed with water and saturated aqueous sodium chloride and dried. Removal of solvent gave a crystalline residue (183 mg) from which two components were isolated by preparative thin layer chromatography on two silica plates (20 × 20 × 0.1 cm) with four elutions with 5% ether in petroleum ether. The major product (145 mg, 83%) was **13**, which was recrystallized from methanol to give colorless needles (104 mg): mp 83–84° (lit.[12] mp 83.5–84.5°); $\lambda_{max}^{CCl_4}$ 5.84 μ; δ^{CCl_4} 0.98 (s, 9 H), 3.11 (d, J = 7 Hz, 2 H), 4.65 (t, J = 7 Hz, 1 H), 7.18 (s, 10 H); *m/e* 266 (4%). A second, minor product (10 mg, 5%) was obtained as a gum, which on crystallization from methanol gave **14** as colorless, fine needles (4.5 mg), mp 89–94° (lit. mp 94–95°). Although it was not obtained pure, its identity was established by a mixture melting point and spectroscopic comparison with an authentic sample.[1]

Action of Sodium Methoxide on 11. Failure to form 10. Compound **11** (58 mg, 0.16 mmol) in ether (10 ml) was treated with sodium hydride (26 mg of a 53.8% dispersion in paraffin; 0.58 mmol) and 4 drops of methanol for 8 days, and the crude product (56 mg) was chromatographed on silica as in the case of the treatment of **10** with sodium methoxide. Elution with petroleum ether and 5 and 10% ether in petroleum ether gave only paraffin from the sodium hydride dispersion. Elution with 20% ether in petroleum ether gave **11** (44 mg). The pmr spectrum of the product gave no evidence for the presence of **10**.

1-(1-Naphthyl)-2,2,4-triphenyl-1,4-butanedione (16). The lactone **9** (1.065 g, 3.41 mmol) in ether (10 ml) was treated with a solution of 0.354 *M* 1-naphthyllithium [prepared from *n*-butyllithium in hexane (Foote) and 1-bromonaphthalene in ether; 10.6 ml, 3.75 mmol], and the reaction mixture was worked up as in the case of the preparation of **10** from **9**. The crude product (1.69 g) was crystallized from methanol to give small prisms (1.11 g, 74%), mp 157.5–159°. When these were recrystallized from methanol, small prisms (910 mg) were obtained with mp 184.5–186°; the infrared spectra of the lower and higher melting forms in solution were identical, indicating that they were dimorphs of **16**. Two further recrystallizations from methanol gave an analytical sample, mp 185–185.5°.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 87.03; H, 5.44.

Reaction of 16 with Sodium Methoxide. Formation of 4-(1-Naphthyl)-1,2,2-triphenyl-1,4-butanedione (17). Compound **16** (206 mg, 0.47 mmol) in ether (150 ml) was treated with sodium hydride (136 mg of a 53.8% dispersion in paraffin; 3.18 mmol) and meth-

(10) R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391 (1969).

(11) The incomplete conversion in this case is attributable to quenching of the reaction by entry of moisture, due to a fall in the nitrogen pressure.

(12) H. H. Weinstock, Jr., and R. C. Fuson, *J. Amer. Chem. Soc.*, **56**, 1241 (1934).

anol (5 drops) in the usual manner for 3 days. The crude product (252 mg), which was a colorless solid, was combined with the crude product (60 mg) from a similar reaction of **16** (52 mg, 0.12 mmol), and subjected to preparative thin layer chromatography on four silica plates (20 × 20 × 0.125 cm) with 13 elutions with 5–12% of ether in petroleum ether. Two compounds were isolated, the minor one being **16** (19 mg, 7%). The major product (205 mg) was a crystalline solid, which was recrystallized from methanol to give **17** as small prisms (192 mg, 74%), mp 165–166°, unchanged on further crystallization from methanol.

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49. Found: C, 86.90; H, 5.50.

Equilibration of 16 and 17 with Sodium Methoxide. Samples of compounds **16** (43 mg) and **17** (34 mg) were separately treated in ether with sodium hydride and methanol in the usual manner for 4 days. The crude products were chromatographed on silica columns as before to remove the paraffin from the sodium hydride dispersion. The mixtures of **16** and **17** eluted with 20–50% ether in petroleum ether were analyzed by pmr spectroscopy. In $CDCl_3$ solution the methylene proton signals of **16** and **17** were too close-lying ($\Delta\nu$ = 2.5 Hz at 60 MHz) to permit quantitative analysis; however, in C_6D_6 solution their separation was increased ($\Delta\nu$ = 7 Hz at 60 MHz) and they could be used for such analysis. The product ratio, **16**:**17**, from **16** was 23:77, while that from **17** was 15:85.

2,2,4-Triphenyl-1-(*p*-tolyl)-1,4-butanedione (18). The lactone **9** (802 mg, 2.57 mmol) in ether (30 ml) was treated with 0.765 *N* *p*-tolyllithium in ether–hexane [prepared from *p*-bromotoluene and *n*-butyllithium (Foote); 4.2 ml, 3.21 mmol] in the usual manner. The crude product was crystallized from methanol to give **18** as needles (652 mg, 63%), mp 160–162°; a second crop (109 mg), mp 158–160°, raised the yield to 73%. Several recrystallizations from methanol gave an analytical sample, mp 163.5–164°.

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.80; H, 5.98.

4-Hydroxy-2,2-diphenyl-4-(*p*-tolyl)-3-butenoic Acid Lactone (20). 2-Diazo-4′-methylacetophenone was prepared from *p*-toluoyl chloride and diazomethane in ether in the usual manner; the crude product was crystallized from hexane to give fine yellow needles (78%), mp 46–49°; a second crystallization from hexane gave the product (67%): mp 48–51° (lit.[13] mp 49–51°); $\lambda_{max}^{CCl_4}$ 4.82, 6.17, 7.43 μ; δ^{CCl_4} 2.40 (s, 3 H), 5.85 (s, 1 H), 7.15 (d, J = 8.5 Hz, 2 H), 7.60 (d, J = 8.5 Hz, 2 H).

(13) A. R. Daniewski and T. Urbański, *Rocz. Chem.*, **42**, 289 (1968).

The lactone **20** was prepared from 2-diazo-4′-methylacetophenone (1.40 g, 8.75 mmol) and diphenylketene[10] (1.90 g, 9.19 mmol) in ether (20 ml) by the procedure used for the preparation of lactone **9**[1] except that the reaction solution was stirred for 18 hr at room temperature and the residue after removal of the ether was heated for 1 hr on the steam bath. The crude product was combined with that from a similar reaction of the diazo ketone (189.5 mg, 1.18 mmol) with diphenylketene (255 mg, 1.31 mmol) and chromatographed on silica (400 g) packed in petroleum ether. The product was introduced onto the column in hot petroleum ether, and when the column had cooled elution was continued with petroleum ether containing increasing proportions of ether. The crude lactone **20** (2.46 g, 76%) was eluted with 8% ether in petroleum ether; two recrystallizations from methanol gave large needles (1.53 g), mp 152–153°. Two further recrystallizations from methanol followed by one from heptane gave an analytical sample: mp 152–152.5°; $\lambda_{max}^{CCl_4}$ 5.58, 6.07 (m); δ^{CDCl_3} 2.36 (s, 3 H), 6.27 (s, 1 H), 7.33 (m, 12 H), 7.58 (d, J = 8 Hz, 2 H); *m/e* 326 (7%).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.51; H, 5.65.

1,2,2-Triphenyl-4-(*p*-tolyl)-1,4-butanedione (19). The lactone **20** (503 mg, 1.54 mmol) in ether (35 ml) was treated with 1.15 *N* phenyllithium in ether–hexane (1.5 ml, mmol) in the usual manner. The crude product (580 mg), which was a colorless crystalline solid, was combined with that from a similar reaction of **20** (93 mg, 0.29 mmol) and recrystallized from methanol to give **19** as fine flakes, contaminated with a small amount of **20** as needles. The latter were removed by hand-picking to give **19** (474.5 mg, 64%), mp 153–155°. Several recrystallizations from methanol gave an analytical sample, mp 155–155.5°.

Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 85.97; H, 5.95.

Equilibration of 18 and 19 with Sodium Methoxide. Samples of compounds **18** (55 mg) and **19** (53 mg) were separately treated in ether with sodium hydride and methanol in the usual manner for 1 week. The mixtures of **18** and **19** thus obtained were analyzed by pmr spectroscopy. In $CDCl_3$ solution the methyl proton signals of **18** and **19** at δ 2.21 and 2.32, respectively, were utilized for this analysis. The product ratio, **18**:**19**, from **18** was 38:62, while that from **19** was 39:61. The mixtures could not be resolved by thin layer chromatography.

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Mechanism of the Rearrangement of Alkyl Phenyl Ethers. Aluminum Chloride Catalyzed Rearrangement of *n*-Butyl and *sec*-Butyl Phenyl Ethers

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Abstract: The neat rearrangement of *n*-butyl phenyl ether (I) using $AlCl_3$ at 0–5° gave rise to ring *n*-butylated and *sec*-butylated I and the corresponding phenols. Similarly, rearrangement of *sec*-butyl phenyl ether (II) with half-molar amounts of catalyst was found to give higher ortho/para ratios than those with equimolar amounts. These results are mechanistically interpreted.

In the course of a study of the rearrangement of optically active butyl phenyl ethers[2] catalyzed by $AlBr_3$ in solvents, an investigation of the neat rearrangement of *n*-butyl and *sec*-butyl phenyl ethers (I and II, respectively) with $AlCl_3$ seemed appropriate. Rearrangements of the latter sort have been reported to be largely intermolecular.[3] However, much earlier, Smith[4] had reported that the rearrangement of I with $AlCl_3$ gave a

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(3) M. J. S. Dewar and N. A. Puttnam, *J. Chem. Soc.*, 4080 (1959).

(4) R. A. Smith, *J. Amer. Chem. Soc.*, **56**, 1419 (1934).