Tetrahedron Vol. 39, No. 13, pp. 2259 to 2263, 1983
Printed in Great Britain

0040-4020/83 $3.00 + .00
Pergamon Press Ltd.

REACTIONS OF α-DIAZO-KETONES—V

ETHER OXYGEN PARTICIPATION IN THE ACETOLYSIS OF α′-PHENOXY- AND α′-DIPHENYLMETHOXY-α-DIAZO-KETONES

A. PUSINO, V. ROSNATI* and C. SOLINAS
Istituto di Chimica Organica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy

and

U. VETTORI
Istituto di Chimica, Politecnico di Milano, Centro CNR per lo Studio delle Sostanze Naturali, p.zza Leonardo da Vinci 32, I-20133 Milano, Italy

(*Received in UK 2 August* 1982)

Abstract—The acetolyses of α-diazo-ketones **1a–d**, **2** and **3a**, **b**, **c** have been studied. The results obtained for **1a–d** indicate that migration of the phenoxy group represents an important, alternative pathway to normal substitution only if a tertiary carbonium ion or a cyclic transition state, with the incipient positive charge located on a tertiary C atom, is involved in the reaction.

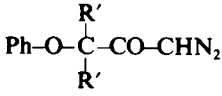
Normal substitution was the only process in the case of **2** and **3a**; instead, **3b** and **3c** gave in addition diphenylmethyl acetate and the corresponding 2-substituted-3-oxetanone, **17** and **19**, produced by a cyclic mechanism involving the intermediate formation of oxonium ions **26b** and **26c**, respectively.

Neighbouring group participation by divalent S is a general feature in the acetolysis of α′-arylthio-α-diazo-ketones and proceeds through a cyclic sulphonium ion.[1-3] The acetolysis of α-diazo-ketone **1a**, labelled ^{13}C at the carbon bearing the diazo group, proved that the phenoxy group does not participate in the reaction, the resulting acetoxy-ketone **4** showing no ^{13}C-labelling distribution.[1] This result could be interpreted on the basis of the low nucleophilicity of the O attached to the aromatic ring, owing to resonance interactions with the π-system. Yet, neighbouring group participation by aryloxy group in solvolytic reactions of α-diazo-ketones, although rare, has been reported. The first example is the acetolysis of α-diazo-*o*-methoxyacetophenone to coumaranone,[4] which was subsequently interpreted as occurring through Ar-0-5-participation,[5] the geometry of the system favouring ring closure rather than direct attack on the diazonium ion by the solvent, as in the case of simple diazo-ketones. However, the most pertinent example is the acid catalyzed rearrangement in the methanolysis of 3-(4-biphenylyloxy)-1-diazo-3-methyl-2-butanone to 1-(4-bi-phenyloxy)-3-methyl-3-buten-2-one, which was interpreted as resulting from Ar-0-4 participation.[6] The latter result suggested that in solvolytic reactions of α′-aryloxy-α-diazo-ketones a 1,3-shift of the aryloxy group might be favoured by substitution at the α′-C. In order to check this hypothesis the acetolyses of α-diazo-ketones **1b**, **1c**, **1d**, structurally related to **1a**, were investigated. Moreover, since the benzyloxy group is frequently encountered in displacement reactions involving neighbouring group participation,[7] the investigation was extended to the acetolysis of α-diazo-ketones **2**, **3a**, **b**, **c** having a more nucleophilic ether O on the α′-C atom.

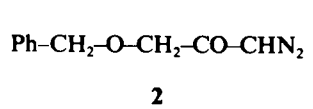
RESULTS AND DISCUSSION

The main results are reported in Table 1. The first observation which stems from these acetolyses is that α-diazo-ketones bearing an ether O on the α′-C, independently from its nucleophilicity, selectively undergo normal substitution, provided no substituent is present on the same carbon. This is shown by the acetolyses of **1a**, **2** and **3a**.

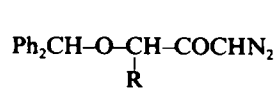
In fact, as previously observed in the case of **1a**,[1] the acetolysis of **2** and **3a**, selectively ^{13}C-labelled at the methinic C, afforded the corresponding acetoxy-ketones **13** and **14** as the only products, with full retention of the initial labelling. Thus, in spite of the more nucleophilic character of the ether O, 0-4 participation either does not occur in these ace-



1a: R′=R″=H
1b: R′=H; R″=CH_3
1c: R′=R″=CH_3
1d: R′=H; R″=Ph

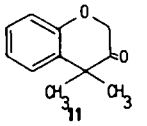
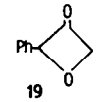


2



3a: R=H
3b: R=CH_3
3c: R=Ph

Table 1. Acetolysis of α-diazo-ketones bearing an ether oxygen on the α′-carbon

SUBSTRATE	PRODUCTS
1a	Ph-O-CH_2-CO-CH_2OAc (100%) **4**
1b	Ph-O-CH(CH_3)-CO-CH_2OAc (96%) **5**; Ph-O-CH_2-CO-CH=CH_2 (2%) **6**; Ph-O-C(=CH_2)-CO-CH_3 (2%) **7**
1c	Ph-O-C(CH_3)$_2$-CO-CH_2OAc (33%) **8**; Ph-O-CH_2-CO-C(CH_3)=CH_2 (50%) **9**; Ph-O-CH_2-CO-C(CH_3)$_2$-OAc (13%) **10**;  (4%) **11**
1d	Ph-O-CH(Ph)-CO-CH_2OAc (100%) **12**
2	Ph-CH_2-O-CH_2-CO-CH_2OAc (100%) **13**
3a	Ph_2CH-O-CH_2-CO-CH_2OAc (100%) **14**
3b	Ph_2CH-O-CH(CH_3)-CO-CH_2OAc (44%) **15**; Ph_2CH-O-CO-CH_3 (56%) **16**;  **17**
3c	Ph_2CH-O-CH(Ph)-CO-CH_2OAc (72%) **18**; Ph_2CH-O-CO-CH_3 (28%) **16**;  **19**

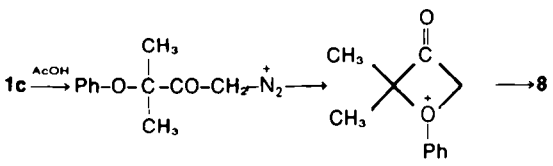
tolyses, or if it does, no σ-bond is formed between the O and the C bearing the leaving group.

Indeed, there is evidence in the literature that a neighbouring oxygenated group needs not form a completely covalent bond with the electrophilic C of the substrate in order to lend anchimeric assistance.[8-11]

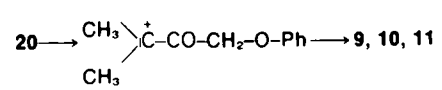
The acetolyses of **1b** and **1c** show instead that, if Me groups are present on the C bearing the ethereal O, rearrangement involving 1,3-shift of the phenoxy group may occur to a minor or greater extent. Thus, while in the case of **1b** only traces of α,β-unsaturated ketone **6** revealed the above rearrangement,† in the case of **1c** normal substitution accounted for only one third of the reaction, the remaining two-thirds resulting in formation of α,β-unsaturated ketone **9**, acetoxy-ketone **10** and chromanone **11**.

The latter acetolysis can be interpreted through Ph-O-4 participation involving a true σ-bond between the O and the electrophilic C of the protonated diazo-ketone; the intermediate oxonium ion **20** might, in fact, undergo nucleophilic attack by the acetate, affording **8**, or collapse to tertiary carbonium ion **21**, which would then deprotonate to **9**, or solvolyze to **10**, or eventually undergo intramolecular electrophilic substitution leading to chromanone **11**.

Alternatively, the participation operating for **1c** might simply involve coordination of the ether O to the electrophilic center, in a process competing with normal substitution. The observed shift of the phenoxy group leading to **9** and **10** would then occur through a concerted mechanism involving a 4-membered transition state. However, chromanone



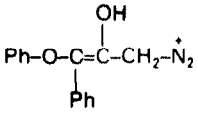
20



21

†The isomeric α,β-unsaturated ketone **7**, most probably was formed from some impurity of 1-chloro-3-phenoxy-2-butanone present in the starting material; indeed, the acetolysis of the latter has been shown to afford **7**.[12]

11 is likely to be formed through a cationic intermediate such as **21**. The pathway leading to migration of the phenoxy group should be characterized in any case by an activation energy closely dependent on the relative stability of either the intermediate cationic species or the transition state leading to the products. This may account for the fact that **1a**, **2** and **3a** did not undergo any rearrangement, since in any case a positive charge would have to be developed on a primary, rather than on a tertiary C atom, as with **1c**. The same argument may hold to a lesser extent also in the case of **1b**. However, the lack of any rearrangement in the acetolysis of **1d** is rather difficult to explain, since a 1,3-shift of the phenoxy group would lead to a stable benzylic cation. One possible explanation is that the acetolysis of **1d** does not involve the protonated diazo-ketone, as in other substrates, but its enolic form **22**, in which extensive conjugation is responsible for selective substitution on the allylic diazonium cation.



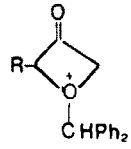
22

The acetolyses of α-diazo-ketones **3a**, **b**, **c**, structurally related to **1a**, **b**, **d**, respectively, present doubts concerning whether neighbouring group participation by the ether is operating in these solvolyses and or whether normal substitution proceeds through an intermediate oxonium ion. This study resulted from the related S analogue **23**, which was shown to undergo acetolysis in neat AcOH affording 30% 1-acetoxy-3-benzydrylthio-2-propanone, **24**, and 70% diphenylmethyl acetate and 3-thia-cyclobutanone, **25**.[9,13]

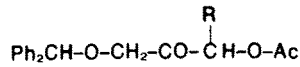
Also, the acetolysis of **23**, selectively ^{13}C-labelled at the C bearing the diazo group, excluded any isotope distribution between the two carbons adjacent to the carbonyl of **24**. These results proved that an open chain mechanism and a cyclic one were operating in the acetolysis of **23** and that neighbouring group participation by the S, if present, did not involve formation of a σ-bond in the process leading to **24**.

The acetolysis of **3a** ^{13}C-labelled at the methinic C led exclusively to acetoxy-ketone **14**, with full retention of the initial labelling, which proves that oxonium ion **26a** was not involved in the reaction. However, normal substitution accounted for only 44 and 67%, respectively, in the acetolysis of **3b** in neat AcOH and in the presence of AcOK, diphenylmethyl acetate and 2-methyl-3-oxetanone, **17**, being clearly formed by the agency of oxonium ion **26b**.†

†Nucleophilic attack at the benzydryl C of **3b** leading to **16** can be excluded, since 1-diphenylmethyl-2-propanone did not undergo acetolysis both in neat AcOH and in the presence of acetate.



26a. R = H
26b. R = CH_3
26c. R = Ph



27a. R = CH_3
27b. R = Ph

Likewise, **26c** must be the precursor of diphenylmethyl acetate and 2-phenyl-3-oxetanone, **19**, obtained in the acetolysis of **3c** in addition to acetoxy-ketone **18**, normal substitution being in this case predominant (72%) even in plain AcOH. Since acetoxy-ketones **27a** and **27b** were not formed in the acetolyses of **3b** and **3c**, respectively, it seems reasonable to conclude that also with the latter substrates, as in the case of **3a**, normal substitution occurred through an open chain mechanism, in which neighbouring group participation, if active at all, might only involve coordination of the ether O to the C bearing the diazo group.

The observed fragmentation, which evidenced neighbouring group participation in the cases of **3b** and **3c**, can be attributed to the presence of a strongly electrophilic C attached to the ether O. Finally, it is remarkable that in both series of α-diazo-ketones **1** and **3**, independently from the nucleophilicity of the ether O, the presence of substituents on the α′-C is determinant in allowing alternative pathways to normal substitution by involving cyclic transition states (as most probably in the cases of **1b** and **1c**) or intermediates (as in the cases of **3b** and **3c**).

EXPERIMENTAL

All m.ps were determined on a Büchi apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer using TMS as the internal standard. The mass spectral data were measured on a Perkin–Elmer 270 spectrometer, directly connected to a gas chromatograph, operating at 80 eV (80 μA). Column: SE 30, 5% on Chromosorb P-80-100 mesh, silanized, temperature: 155°; injector temperature: 250°; manifold temperature: 200°; ion source temperature: 200°. Carrier gas: He, 15 ml min^{-1}.

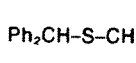
All the substrates were prepared starting from the appropriate acyl chloride by reaction with an ether soln of CH_2N_2 (mole ratio 1:4). After the usual work-up, the oily residue was taken into ether–hexane and chromatographed on silica gel (eluant $CHCl_3$) in order to eliminate the impurity of the corresponding α-chloroketone.

1-*Diazo*-3-*phenoxy*-2-*butanone*, **1b**; crystals, m.p. 31–2°. NMR (CCl_4), δ: 7.33–6.66 (5H, m); 5.50 (1H, s); 4.55 (1H, q); 1.50 (3H, d).

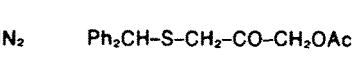
1-*Diazo*-3-*phenyl*-3-*phenoxy*-2-*propanone*, **1c**; oil, NMR ($CDCl_3$), δ: 7.66–6.76 (10H, m); 5.76 (1H, s); 5.56 (1H, s).

1-*Diazo*-3-*methyl*-3-*phenoxy*-2-*butanone*, **1d**; crystals, m.p. 63°. NMR (CCl_4), δ: 7.26–6.60 (5H, m); 5.58 (1H, s); 1.46 (6H, s).

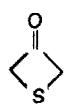
1-*Diazo*-3-*benzyloxy*-2-*propanone*, **2**; oil, NMR (CCl_4), δ: 7.16 (5H, s); 5.58 (1H, s); 4.46 (2H, s); 3.38 (2H, s).



23



24



25

Chromatography of the crude product allowed isolation of pure **2** and, as a by-product, of 1-benzyloxy-2-chloromethyl-2,3-epoxypropane, oil, NMR (CCl_4), δ: 7.13 (5H, s); 4.46 (2H, s); 4.00–3.26 (4H, m); 2.63 (2H, s). MS, *m/z* (%): 214(0.2), $M^{+\cdot}$ 212(0.5), 149(1), 108(6), 107(60), 106(10), 105(34), 93(2), 92(15), 91(100), 90(2), 89(5), 80(2), 79(30), 78(5), 77(18), 75(3), 71(5), 65(25), 64(2), 63(7), 57(5), 53(2), 52(3), 51(11), 50(4), 49(7), 44(1), 43(4), 42(5), 41(10), 40(3), 39(20), 38(2), 37(1), 36(4).

1-*Diazo*-3-*diphenylmethoxy*-2-*propanone*, **3a**; crystals, m.p. 61–2°. NMR (CCl_4), δ: 7.30 (10H, s); 5.70 (1H, s); 5.33 (1H, s); 3.93 (2H, s).

1-*Diazo*-3-*diphenylmethoxy*-2-*butanone*, **3b**; crystals, m.p. 55–6°. NMR (CCl_4), δ: 7.33–7.00 (10H, m); 5.61 (1H, s); 5.33 (1H, s); 3.83 (1H, q); 1.30 (3H, d).

1-*Diazo*-3-*diphenylmethoxy*-3-*phenyl*-2-*propanone*, **3c**; oil, NMR (CCl_4), δ: 7.40–6.83 (15H, m); 5.63 (1H, s); 5.33 (1H, s); 4.65 (1H, s).

General procedure for the acetolysis. The acetolyses were performed on approx. 1–2 mmol, both in neat AcOH and, occasionally, in the presence of AcOK, under standard conditions (substrate concentration: 0.2 M; AcOK concentration 0.6 M; temp 114°; reaction time 5 min). The cold soln of the substrate in AcOH was rapidly added to boiling AcOH or AcOH–AcOK soln. The crude mixture was quenched and treated twice with H_2O (10 ml) and CCl_4 (20 ml). After shaking, the CCl_4 solns were dried over $MgSO_4$, filtered and evaporated. NMR, GC and GC/MS analyses were performed on the residues.

Acetolysis of **1b**. The reaction in plain AcOH and in the presence of AcOK gave practically the same results. GC/MS analysis showed the composition reported in Table 1. Acetoxy-ketone, **5**, was purified by column chromatography on silica gel (oil b.p. 143°, 0.3 mm Hg). Compounds **6** and **7** were not isolated in pure state; their identification was made by GC/MS spectrometry.

1-*Acetoxy*-3-*phenoxy*-2-*butanone*, **5**: NMR (CCl_4), δ: 7.33–7.66 (5H, m); 4.80 (2H, AB System); 4.83 (1H, q); 2.05 (3H, s); 1.50 (3H, d). MS, *m/z* (%): $M^{+\cdot}$ 222(3), 129(2), 121(100), 115(1), 107(1), 103(1), 101(2), 94(3), 93(4), 91(1), 78(1), 77(14), 65(3), 51(4), 43(20), 39(3).

1-*Phenoxy*-3-*buten*-2-*one*, **6**: MS, *m/z* (%): $M^{+\cdot}$ 162(22), 134(8), 133(8), 119(22), 105(4), 94(100), 91(32), 90(2), 89(3), 78(5), 77(20), 66(73), 65(40), 55(7), 51(16), 43(40), 40(20), 39(60).

3-*Phenoxy*-3-*buten*-2-*one*, **7**†: MS, *m/z* (%): $M^{+\cdot}$ 162(21), 119(31), 94(15), 92(6), 91(64), 78(6), 77(62), 66(6), 65(14), 51(22), 43(100), 39(10).

Acetolysis of **1c**. GC/MS and NMR analysis of the crude reaction mixture showed practically the same composition in plain AcOH and in the presence of AcOK (Table 1). Acetoxy-ketones **8** and **10** and α,β-unsaturated ketone **9** were isolated in pure state by column chromatography over silica gel. Chromanone **11** was only detected by GC/MS analysis; this technique showed that **11** was not a chromatographic artefact deriving from **9**.‡ Acetoxy-ketone **10** was shown to be stable under the experimental conditions employed for the GC analysis.

1-*Acetoxy*-3-*methyl*-3-*phenoxy*-2-*butanone*, **8**: oil; NMR (CCl_4) δ: 7.32–6.66 (5H, m); 4.96 (2H, s); 2.08 (3H, s); 1.46 (6H, s). MS, *m/z* (%): $M^{+\cdot}$ 236(2), 176(1), 135(100), 108(2), 107(13), 101(6), 95(30), 94(32), 91(3), 79(2), 78(3), 77(33), 73(2), 70(3), 69(4), 66(5), 65(7), 55(4), 51(13), 50(2), 44(2), 43(80), 42(10), 41(22), 40(4), 39(12).

1-*Phenoxy*-3-*methyl*-3-*buten*-2-*one*, **9**. (Oil b.p. 140–2° 1 mm Hg). NMR (CCl_4) δ: 7.26–6.56 (5H, m); 5.98 (1H, m); 5.71 (1H, m); 4.73 (2H, s); 1.85 (3H, m). MS, *m/z* (%): $M^{+\cdot}$ 177(8), 176(60), 148(10), 134(3), 133(34), 108(3), 107(28), 94(10), 83(20), 79(22), 78(8), 77(85), 70(5), 69(100), 66(4), 65(11), 63(5), 55(25), 51(34), 50(5), 42(5), 41(90), 40(5), 39(37).

3-*Acetoxy*-3-*methyl*-1-*phenoxy*-2-*butanone*, **10**; (oil b.p. 108–10°, 0.3 mm Hg). NMR (CCl_4) δ: 7.26–6.60 (5H, m); 4.63 (2H, s); 2.00 (3H, s); 1.50 (6H, s). MS, *m/z* (%): $M^{+\cdot}$ 236(10), 210(2), 178(7), 176(2), 165(10), 150(4), 143(8), 135(80), 129(18), 108(7), 107(26), 101(28), 95(10), 94(12), 79(5), 78(3), 77(30), 69(5), 65(5), 64(3), 59(50), 55(5), 51(10), 50(3), 44(10), 43(100), 41(10), 39(10).

4,4-*Dimethyl*-*chroman*-3-*one*, **11**; MS, *m/z* (%): 177(15), $M^{+\cdot}$ 176(90), 161(30), 135(15), 134(33), 133(100), 121(8), 119(10), 117(7), 115(15), 105(90), 103(12), 94(60), 91(20), 77(30), 65(15), 63(10), 57(12), 55(15), 51(25), 44(60), 43(50).

Acetolysis of **1d**. The acetolysis in plain AcOH, as well as in the presence of AcOK, afforded **12** as the only product: (oil b.p. 140–2° at 0.2 mm Hg). NMR (CCl_4) δ: 7.46–6.76 (10H, m); 5.56 (1H, s); 4.93 (2H, s); 2.06 (3H, s). MS, *m/z* (%): $M^{+\cdot}$ 284(1), 196(1), 195(1), 194(1), 191(2), 184(16), 183(100), 165(3), 156(3), 155(30), 154(2), 153(3), 152(1), 151(1), 149(2), 148(2), 132(2), 131(12), 129(2), 128(2), 127(1), 121(1), 120(1), 119(1), 118(3).

Acetolysis of **2**. The reaction was run only in plain AcOH. NMR and GC/MS analysis showed the formation of **13** (oil, b.p. 97–8°, 1 mm Hg) as the only reaction product. NMR (CCl_4) δ: 7.16 (5H, s); 4.56 (2H, s); 4.50 (2H, s); 4.00 (2H, s); 2.10 (3H, s). MS, *m/z* (%): $M^{+\cdot}$ 179(0.2), 162(0.2), 150(1), 149(0.5), 135(0.5), 117(1), 116(11), 108(1), 107(23), 105(1), 104(1), 101(7), 92(11), 91(100), 90(2), 89(4), 79(4), 77(5), 74(11), 73(10), 65(10), 63(3), 52(1), 51(4), 50(1), 43(49), 42(2), 41(2), 39(5).

Acetolysis of **3a**. Both acetolyses in plain AcOH and in the presence of AcOK gave **14** (crystals m.p. 86–7°) as the only product. NMR (CCl_4) δ: 7.43–7.10 (10H, m); 5.35 (1H, s); 4.83 (2H, s); 4.00 (2H, s); 2.06 (3H, s).

Acetolysis of **3b**. The final soln of the acetolysis in plain AcOH was concentrated by distillation using an efficient column; the first fraction (0.6 ml) when submitted to GC/MS analysis revealed the presence of two products having molecular peaks 86 and 84, respectively. The first compound, the minor component of the mixture, was identified as **17**.§ MS, *m/z* (%): $M^{+\cdot}$ 86(18), 71(8), 57(95), 56(87), 43(100), 42(35), 41(90), 39(20), 29(30).

The structure of the other component, possibly a gas-chromatographic artefact, was not established.

The concentrated AcOH solution was diluted with CCl_4 (20 ml) and treated with a sat $NaHCO_3$ aq; the organic layer, after drying and removal of the solvent, left an oil having the following composition (NMR analysis): 56% diphenylmethyl acetate, 44% **15**. NMR (CCl_4) δ: 7.50–7.10 (10H, m); 5.40 (1H, s); 4.80 (2H, s); 3.93 (1H, q); 2.05 (3H, s); 1.50 (3H, d). When the above acetolysis was performed in the presence of 0.6 M AcOK, after removal of the solvent, NMR analysis of the crude reaction mixture gave 67% **15**, 33% diphenylmethyl acetate.

3-*Diphenylmethoxy*-2-*butanone*. In a 3-necked flask equipped with magnetic stirrer, dropping funnel, reflux

†The assignment of structure **7** is based on the fragmentation observed in the mass spectrum; in particular, the latter shows the acetyl ion (*m/z* 43) much more intense than in the spectrum of the isomeric compound **6**. The ion with *m/z* 134, which is absent in the mass spectrum of **7**, could originate from **6** through a primary loss of CO.

‡By comparing the mass spectra of the isomeric **9** and **11**, the following observations can be made. Compound **9** shows the characteristic fragmentations due to the bond breaking in α to the CO (*m/z* 41, 69 and 107) and to the ethereal linkage (*m/z* 83 and 94). The ions with *m/z* 148 and 133 are derived from the molecular ion by loss of CO (determination of the exact mass) and $CO + CH_3$, respectively. The formation of these ions must involve a cyclization, however not to compound **11**. The latter, in fact, does not show a primary loss of CO (*m/z* 148 is absent), but consecutive losses of CH_3 and CO (*m/z* 161 and 133), while ions typical of **9** (*m/z* 41, 69, 83 and 107) are absent.

§The assignment of structure **17** is based on the presence of the molecular ion (*m/z* 86) and of the fragments with *m/z* 71 ($M-CH_3$), 56 ($M-CH_2O$) and 43 (CH_3CO^+).

condenser and inlet tube for N_2, 0.4 g of 2-diphenylmethoxy propionic acid were slowly treated with a 5% ethereal suspension of MeLi (4 ml). The mixture was left for 20 hr at 25°. After the usual work-up the ethereal soln gave 0.35 g of crude product. A sample, after purification by chromatography over silica gel, gave crystals of title compound m.p. 51–52°. NMR (CCl_4) δ: 7.20 (10H, s); 5.28 (1H, s); 3.77 (1H, q, J = 6 Hz); 2.07 (3H, s); 1.32 (3H, d, J = 6 Hz). MS, *m/z* (%): 211(0.5), 210(0.1), 184(3), 183(22), 182(2), 169(1), 168(14), 167(100), 166(10), 165(25), 164(3), 163(2), 153(2), 152(12), 151(1), 139(2), 128(2), 115(2), 105(5), 89(1), 77(5), 72(1), 65(1), 63(1), 51(3), 43(7), 39(1).

The above ketone was recovered unchanged after 30′ refluxing in the AcOH/AcOK system.

Acetolysis of **3c**. The reaction was run only in AcOH. GC/MS and NMR analysis of the crude mixture gave the composition reported in Table 1.

1-*Acetoxy*-3-*diphenylmethoxy*-3-*phenyl*-2-*propanone*, **18**, was isolated in pure state by column chromatography over silica gel (eluant 50:1 light petroleum ether–EtOAc): oil b.p. 104–5° at 0.05 mm Hg. NMR (CCl_4) δ: 7.43–6.93 (15H, m); 5.40 (1H, s); 4.81 (2H, AB system); 2.06 (3H, s).

2-*Phenyl*-3-*oxetanone*, **19**, was isolated only in mixture with **18**. NMR (CCl_4) δ: 7.30–7.00 (5H, m); 6.13 (1H, s); 3.95 (2H, s). MS, *m/z* (%): $M^{+\cdot}$ 148(2), 118(0.5), 106(10), 105(100), 104(1), 103(3), 78(8), 77(87), 76(5), 75(4), 74(7), 51(40), 50(14), 43(26), 42(7).

Acknowledgements—The present work was supported by the Italian National Research Council (CNR). The authors wish to thank Mr. Sergio Cossu for experimental assistance.

REFERENCES

[1]S. Gladiali, A. Pusino, V. Rosnati, A. Saba and F. Soccolini, *Gazz. Chim. Ital* **107**, 535 (1977).
[2]A. Pusino, V. Rosnati, A. Saba, F. Soccolini and A. Selva, *Ibid.* **108**, 557 (1978).
[3]W. T. Flowers, A. M. Freitas, G. Holt and S. C. Purkiss, *J. Chem. Soc.* Perkin Trans. I, 1119 (1981).
[4]E. R. Marshall, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.* **7**, 444 (1942).
[5]A. K. Bose and P. Yates, *J. Am. Chem. Soc.* **74**, 4703 (1952).
[6]N. A. Nelson, *J. Org. Chem.* **38**, 3798 (1973).
[7]B. Capon, *Chem. Rev.* **64**, 407 (1969).
[8]D. S. Noyce, B. R. Thomas and B. N. Bastian, *J. Am. Chem. Soc.* **82**, 885 (1960).
[9]D. S. Noyce and B. N. Bastian *Ibid.* **82**, 1246 (1960).
[10]K. C. Kemp and D. Metzger, *J. Org. Chem.* **33**, 4165 (1968).
[11]F. G. Bordwell and A. C. Knipe, *Ibid.* **35**, 2956 (1970).
[12]A. Pusino, V. Rosnati, A. Saba and A. Franco, *Gazz. Chim. Ital.* **112**, 495 (1982).
[13]V. Rosnati and F. Soccolini, *Ibid.* **109**, 623 (1979).