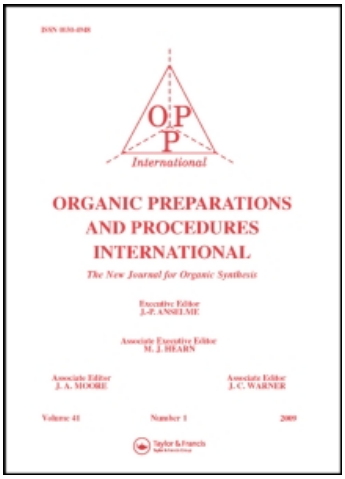

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USE OF DIETHYL PHENYLMALONATE AS A NUCLEOPHILIC DONOR IN THE MICHAEL REACTION[1]

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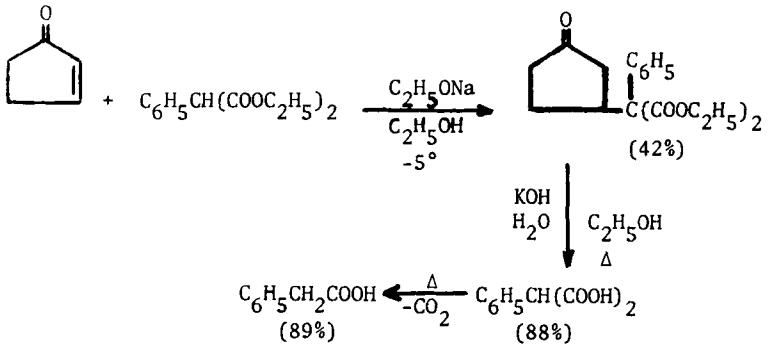

The use of diethyl phenylmalonate as a nucleophilic donor in the Michael reaction has previously been reported to be unsuccessful in reactions with ethyl crotonate,[2] ethyl tiglate (ethyl trans-2-methyl-2-butenoate)[2], ethyl cinnamate,[2] and benzalacetophenone,[2,3] and from these results it was concluded that diethyl phenylmalonate does not undergo the Michael reaction.[2,4] We have found the addition of diethyl phenylmalonate to the reactive acceptor, 2-cyclopenten-1-one, to be successful, however, as it gave diethyl 3-oxo-α-phenylcyclopentanemalonate in 42% yield as a low-melting solid (mp 50-52°), having elemental analyses and an nmr spectrum consistent with the proposed structure. Our reaction conditions were similar to those previously employed for the addition of diethyl malonate to 2-cyclopenten-1-one[5] and 2-cyclohexen-1-one,[6] and involved low temperature (-5°) and the use of sodium ethoxide as catalyst in the

ratio of only 5 mole % of the diethyl phenylmalonate used. These are conditions which would be expected to minimize ethanolysis of diethyl phenylmalonate to ethyl phenylacetate and diethyl carbonate before addition, or of the adduct of diethyl phenylmalonate after addition has taken place. In contrast, in the unsuccessful experiments Connor[2] employed less reactive acceptors at elevated temperatures, in refluxing solvents such as ethanol, benzene, or ether. When sodium ethoxide in ethanol was used in an amount equivalent to the diethyl phenylmalonate, extensive ethanolysis occurred, giving diethyl carbonate and the Michael adduct to be expected from the ethanolysis product, ethyl phenylacetate (or derivable by ethanolysis of an adduct formed initially from diethyl phenylmalonate). Since extensive ethanolysis of diethyl phenylmalonate was also shown to occur with sodium ethoxide in refluxing ethanol in the absence of an acceptor, it was suggested that the observed products were formed from the ethanolysis product, ethyl phenylacetate.[2] In the media other than ethanol, even when less than an equivalent of sodium ethoxide was employed, little or no product was formed, and what was formed could be accounted for by prior ethanolysis of diethyl phenylmalonate.

It was hoped that hydrolysis and decarboxylation of our adduct would give 3-oxo-α-phenylcyclopentaneacetic acid, but, instead all attempts caused reversal of the Michael reaction. For example, alkaline saponification with ethanolic potassium hydroxide gave a polymeric solid (presumed to be a polymer of 2-cyclopenten-1-one) and crude phenylmalonic acid (88%), which decarboxylated during recrystallization to phenylacetic acid (78%). Acidic hydrolysis with 48% hydrobromic acid and acetic acid gave tarry black decomposition products and an acidic oil from which phenylacetic acid (61%) was separated by chromatography or phenylacetamide (57%) was separated by conversion to the acid chloride and treatment with

ammonia.

EXPERIMENTAL

Diethyl 3-Oxo-α-phenylcyclopentanemalonate.- A solution of sodium (0.20 g, 8.7 mg-atoms) in absolute ethanol (70 ml) was cooled to -5° in an ice-salt bath and diethyl phenylmalonate [Eastman Organic Chemicals, ir cm^{-1} (neat) 1724 vs (C=O); 38.5 g, 163 mmol] was added, followed by dropwise addition, with rapid stirring, of 2-cyclopenten-1-one[7] [n_D^{20} 1.4780; ir cm^{-1} (neat) 1695 vs (C=O), 1580 m (C=C); 12.0 g, 146 mmol] over a period of 0.5 hr under nitrogen. The rust-colored solution was stirred for an additional hr at -5°, kept overnight in a freezer, and then acidified with glacial acetic acid (2 ml). The ethanol was removed in a rotary evaporator, giving a viscous yellow oil. Fractional distillation at reduced pressure gave a colorless oil (19.65 g, 42%), bp 151-154° (0.04 mm), n_D^{26} 1.5124; ir cm^{-1} (neat) 3410 w (C=O overtone), 1730 vs (C=O). Upon being kept for 24 hr, the oil solidified to a white solid, mp 50-52°; ir cm^{-1} (Nujol) 3450 vw (C=O overtone), 1751 s and 1733 s (C=O); nmr τ(20% w/w in $CHCl_3$-d) 2.62 (s, 5.0, $C_6\underline{H}_5$), 5.74 (q, 3.8, J=7 Hz, $OC\underline{H}_2CH_3$), 6.72 (bm 1.0, C<u>H</u>), 7.28-8.49 (m, 6.1, $3C\underline{H}_2$), 8.77 (t, 6.1, J=7 Hz, $OCH_2C\underline{H}_3$).

Anal. Calcd for $C_{18}H_{22}O_5$(318.36): C, 67.91; H, 6.97. Found C, 67.98; H, 7.22.

Reverse Michael Addition.- A solution of diethyl 3-oxo-α-phenylcyclopentanemalonate (6.40 g, 20.1 mmol) and potassium hydroxide (22.40 g, 400 mmol) in ethanol (50 ml) and water (100 ml) was kept at room temperature for 45 min. The solution became black immediately and some solid formed near the surface. The mixture was then refluxed on a steam bath for 8 hr (which seemed to increase the amount of solid), cooled, and filtered to remove the resulting very insoluble tan solid (1.40 g), mp

>300°; ir cm^{-1} (Nujol) 3330 m (OH), 1727 s (C=O), 1637 ms (C=O?). The black filtrate was cooled in an ice bath and acidified with concentrated hydrochloric acid. The resulting dark yellow solution was extracted repeatedly with ether and the ether extracts were dried ($MgSO_4$) and evaporated, leaving a yellow oil, which solidified upon cooling and being scratched, giving impure phenylmalonic acid (3.20 g, 88%), mp 120-130° dec; ir cm^{-1} (Nujol) 2670 mw and 2620 mw (OH), 1683 s (C=O); lit.[8] mp 152-153° dec with CO_2 evolution. Two crystallizations from water with charcoal caused a lowering of the mp to 70-74°. Two recrystallizations from petroleum ether (bp 60-68°) gave the decarboxylation product, phenylacetic acid (2.14 g, 78% from the ester), mp 75-76°. There was no depression in mmp, 75-76°, with an authentic sample and the ir spectra in Nujol were identical.

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