prepared by reacting the corresponding pyridazonimines (IIIa and IIIb, respectively) with a large excess of methyl iodide in refluxing benzene for 0.5 h. The resulting suspensions were cooled and filtered to give nearly pure (IVa) and (IVb) directly. The over-all yield of crude (IVb) from the salt (IIb) was 70–75 %. Recrystallization from ethyl acetate-acetonitrile gave the pure salt, m.p. 150–52°. (Found: C 37.39; H 5.90; N 17.46; I 39.29. Calc. for $C_{10}H_{19}N_4I$: C 37.28; H 5.94; N 17.39; I 39.38).

The pyridazonimine IIIc reacted very slowly with excess methyl iodide in refluxing benzene. After 18 h, only about 1/3 of the imine had reacted. Analytical and NMR data of the methiodide (IVc) will be published in another paper.

1. Brewster, J. H. and Eliel, R. L. *Org. Reactions* **7** (1953) 99.
2. Kelstrup, E. *Acta Chem. Scand.* **23** (1969) 1797.
3. Garmaise, D. L. and Paris, G. Y. *Chem. Ind. (London)* **1967** 1645.
4. Landquist, J. K. Communication at the *Deuxième Congres International de Chimie Heterocyclique*, Montpellier, France, July 7–11, 1969.
5. Crossland, I. and Kofod, H. *Acta Chem. Scand.* **21** (1967) 2131.
6. Kofod, H. *Ph. D. Dissertation 1968*, The Technical University, Denmark, in Danish.
7. Lund, H. and Lunde, P. *Acta Chem. Scand.* **21** (1967) 2131.

Received August 20, 1969.

Ion Pair Extraction in Preparative Organic Chemistry

V. Alkylation of Dimethyl Benzoylmalonate

ARNE BRÄNDSTRÖM and ULF JUNGGREN

Chemical Research Laboratory, AB Hässle, Fack, S-402 20 Göteborg 5, Sweden

Methyl ketones are conveniently prepared from a dialkyl malonate by acylation followed by hydrolysis of the intermediate dialkyl acylmalonate.[1] When this method is applied to alkylated dialkyl malonates the yield of the corresponding ketone is often very low due to a competing *O*-acylation in the first step. A logical method would be to alkylate the readily available dialkyl acylmalonates, since alkylation gives a higher yield of *C*-substitution than acylation.[2] The dialkyl acylmalonates, however, are rather strong acids and the corresponding anion thus a weak nucleophile. The alkylation would thus be a very slow process when conventional methods are used. The yields can also be expected to be very low due to side-reactions such as alcoholysis, which is rapid even in the cold.[3]

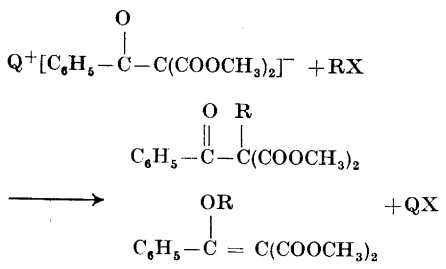
We have recently demonstrated that ion pairs of some enolates are very rapidly alkylated in a chloroform or methylene chloride solution.[4] We will now report that the same method can be used in the present case.

The tetrabutylammonium salt of dimethyl benzoylmalonate is readily extracted by chloroform from a water-solution, containing tetrabutylammonium hydroxide. It forms a crystallized salt, which can be readily alkylated in chloroform or methylene chloride. The alkylation with methyl iodide, for instance, is complete after about 10 min and gives a quantitative yield of dimethyl benzoylmethylmalonate. When the size of the alkyl group is increased the reaction rate is reduced and the yield of *O*-alkylated product increases. With isopropyl iodide *O*-alkylation is the main reaction.

In the present investigation the dimethyl ester was used in order to facilitate the quantitative analysis by NMR. The results are summarized in Table 1 and show the amount of *C*- and *O*-alkylated products in the mixture after alkylating the tetrabutylammonium salt of dimethyl benzoylmalonate.

Table 1.

Alkyl halide	*C*-alkylated product, %	*O*-alkylated product, %
Methyl iodide	100	0
Ethyl iodide	54	46
Butyl iodide	47	53
Isopropyl iodide	14	86



Experimental. Tetrabutylammonium salt of dimethyl malonate. 11.8 g (0.05 mole) of dimethyl benzoylmalonate [5] in 50 ml of chloroform was shaken with a solution containing 17 g (0.05 mole) of tetrabutylammonium hydrogen sulphate (Astra-Meditec) and 4 g (0.1 mole) of sodium hydroxide in 50 ml of water. The chloroform layer was evaporated and the residue recrystallized from ethyl acetate. The yield was 15.5 g (64 %) of a salt melting at 109–110°C.

Alkylation procedure. About 0.05 mole of the tetrabutylammonium salt of dimethyl benzoylmalonate was dissolved in 100 ml of chloroform. An excess of alkyl iodide was added to the stirred solution. The reaction with methyl iodide was exothermic and was complete after a few minutes. With ethyl, isopropyl, and butyl iodides, however, it was necessary to heat to about 55°C for 15–30 min. The chloroform was then evaporated and the tetrabutylammonium iodide was precipitated with ether. The salt was filtered off and the ether evaporated. The residue was analysed by NMR in a chloroform solution.

Acknowledgement. Financial aid from the *Swedish Natural Science Research Council* is gratefully acknowledged.

1. *Org. Syn. Coll. Vol.* **4** (1963) 708.
2. Brändström, A. *Arkiv Kemi* **6** (1953) 159.
3. Dickmann, W. and Wittmann, A. *Ber.* **55** (1922) 3331.
4. Brändström, A. and Junggren, U. *Acta Chem. Scand.* **23** (1969) 2204.
5. *Org. Syn. Coll. Vol.* **4** (1963) 285.

Received August 27, 1967.

Hydrolysis of the Quinol Ether Dimer Obtained on Oxidation of 2,6-Di-*t*-butyl-4-propionylphenol

GÖSTA BRUNOW

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-402 20 Göteborg 5, Sweden

In connection with studies on the biosynthesis and biological decomposition of lignin we are investigating the mechanism of the oxidative cleavage of side-chains from various lignin model compounds. In a recent investigation [1] it was shown that a side-chain containing an α-carbonyl group can be split off from a phenolic model compound by the action of phenol oxidases. It is known [2] that a phenoxy radical is formed as the first product when a phenol is attacked by a phenol oxidase. In a first approach to the study of the reactions of phenoxy radicals carrying an α-carbonyl (or α-carbinol) substituent in the 4-position, the sterically hindered 2,6-di-*t*-butyl-4-propionylphenol (I) was oxidized to a stable free radical and its reactions studied.

This radical in solution is in equilibrium with a dimer which can be isolated as a colourless crystalline compound. This behaviour of (I) is in analogy with that of the corresponding acetyl compound.[3] The dimer dissolves in organic solvents with a deep blue-green colour; an absorption maximum at 700 nm was observed which was strongly temperature dependent, the colour disappearing at low temperatures. At room temperature a strong ESR signal was obtained. The dimer can be ascribed the 2,5-cyclohexadienone structure (II) mainly on the evidence of the NMR spectrum measured at −60° (Fig. 1). Two *t*-butyl peaks at δ 1.10 and 1.35 ppm and the single quinonoid proton peak at 6.14 ppm indicate that the solution at this temperature contained mainly a 2,5-cyclohexadienone.

The dimer (II) proved to be unstable in the presence of dilute mineral acid. At low temperatures, when the concentration of dimer was sufficiently large, the addition of dilute hydrochloric acid gave propionic acid in a rapid reaction. The yields varied with varying temperatures;