determine α and hence, the composition of copolymer resulting from any other monomer mixture. We have recently found that for the system styrene–maleic anhydride α has a value of about 24.

Experimental

Styrene monomer (Dow N-100) and maleic anhydride (Eastman 1226) were copolymerized in solution in thiophene-free benzene, using benzoyl peroxide as catalyst. While the monomer ratio in the charge was varied, the total concentration of monomers was maintained at 2.0 moles per 1500 g. of benzene solution. The mix was refluxed with vigorous stirring. As soon as a small amount of copolymer formed, the batch was cooled and the copolymer filtered. Except in the last two experiments, the copolymer precipitated in the form of very fine white particles. The polymer was purified by boiling three times in benzene in the ratio of 1 part polymer to 50 parts benzene and the yield determined as closely as possible. After exhaustive vacuum drying, the copolymers were hydrolyzed and dissolved in 0.2 N sodium hydroxide. The maleic anhydride content was determined by electrometric titration.

The resulting data are shown in Table I. In equation (2) "A" and "a" stand for styrene monomer and styrene in the initial copolymer, respectively, and "B" and "b" stand for maleic anhydride monomer and maleic anhydride in the initial copolymer.

TABLE I

Monomer		Copolymer				
Mol., % styr.	Mol., % m. a.	Mol., % styr.	Mol., % m. a.	% Yield	α	Calcd. mol. % m. a.
5	95	50.1	49.9	2.8	11.5	49.9
50	50	51.1	48.9	...	21.7	49.0
83.3	16.7	55.0	45.0	1.9	23.0	45.3
90.9	9.1	57.6	42.4	1.7	28.8	41.3
95.0	5.0	65.7	34.3	1.9	22.2	35.8
95.0	5.0	61.1	38.9	2.9	37.5	35.8

In the determination of the constant, the following sources of error are known: (1) When the molecular ratio of styrene to maleic anhydride in the copolymer is close to 1.0, the calculated constant is unreliable, since small errors in maleic anhydride determination cause the value of α to vary enormously. (2) When the concentration of maleic anhydride is very low in the initial charge (see last two runs), we do not obtain a true initial copolymer because the yield necessary for analysis causes a large change in the ratio of the monomers in the charge. However, by calculating from the yield what the monomer ratio is at the end of the reaction and averaging this with the initial monomer ratio, a better value for the monomer ratio in the charge is obtained for the calculation of α. (3) The copolymers of the last two batches did not retain their particle size in boiling benzene but agglomerated to a soft gel-like mass. This could be due to their high styrene content or to low molecular weight. The per cent. maleic anhydride in the last batch, which is a repeat on the next to last batch, differs beyond the experimental error in analysis. A reasonable explanation for this difference is that the purification technique of boiling the resin in benzene is not reliable with a resin which swells in boiling benzene. In view of these sources of error, a reasonable estimate for α would be 24 ± 5. Using $\alpha = 24$, the mole per cent. maleic anhydride in the initial copolymer has been calculated. The results are shown in the last column of Table I and can be compared with the observed values of column 4.

RESEARCH LABORATORIES
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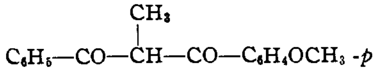
The Methylation of *p*-Methoxy Dibenzoylmethane

BY CHARLES L. BICKEL

In 1926, Bradley and Robinson[1] attempted to methylate *p*-methoxydibenzoylmethane. Their experiments, inadequately described, were unsuccessful and they concluded that the direct methylation of this diketone was not a likely probability. The above authors then condensed ethyl benzoate and *p*-methoxypropiophenone in the presence of sodamide to give a yellow solid, melting at 56.5° and giving both a copper salt and an intense ferric chloride coloration. This compound was assumed to be the methyl derivative of *p*-methoxydibenzoylmethane, I, and the



$$C_6H_5\text{—CO—}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{H—CO—}C_6H_4OCH_3\text{-}p \qquad \text{I}$$

results of alkaline hydrolysis of this substance were compared with those of *p*-methoxydibenzoylmethane itself.

In 1928, Weygand[2] was unsuccessful in an attempt to prepare I by the action of methyl iodide on the sodium derivative of the diketone, using acetone as a solvent. However, the potassium derivative of the diketone, treated with methyl iodide in ether–benzene solution, gave a colorless solid, melting at 72° and giving neither a copper salt nor a ferric chloride coloration. This substance was converted into an enolic compound by the action of sodium methylate and iced sulfuric acid, and the 72° keto form was regenerated by ordinary recrystallization. The 72° compound has the properties which one would ascribe to I while the properties of the 56.5° compound prepared by Bradley and Robinson are not in agreement with the structure of I.

In order to compare unsymmetrical beta diketones with their methyl derivatives,[3] the author recently set out to methylate the beta diketones by means of silver oxide and methyl iodide[4] in anhydrous ether. *p*-Methoxydibenzoylmethane can be methylated in this way with no more difficulty than is experienced in the case of dibenzoylmethane, except for the fact that *p*-methoxydibenzoylmethane is much more insoluble in ether and tends to crystallize on the walls of the flask above the boiling ether. Acetone was therefore substituted for ether as the solvent and the above difficulty was overcome.

The chief product of the reaction of methyl iodide with *p*-methoxydibenzoylmethane in the presence of silver oxide is the 72° compound previously reported by Weygand. The yield is at least as good and the method is much simpler.

The identity of the substance prepared by Bradley and Robinson is as yet obscure but it is

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(1) Bradley and Robinson, *J. Chem. Soc.*, **129**, 2360 (1926).

(2) Weygand, *Ber.*, **61**, 688 (1928).

(3) As yet unpublished.

(4) Abell, *J. Chem. Soc.*, **101**, 992 (1912).

most certainly not the methyl derivative of *p*-methoxydibenzoylmethane.

Experimental

A mixture of 2 g. of *p*-methoxydibenzoylmethane (m. p. 132°, prepared from the dibromide of benzal-*p*-methoxyacetophenone by the action of alcoholic potassium hydroxide followed by acidification), 2 g. of dry silver oxide, 50 cc. of dry ether and 8 g. of methyl iodide was refluxed for six hours, filtered, evaporated to a small volume and low-boiling petroleum ether added to faint turbidity. The yield was 1.7 g. (80%), m. p. 72°. The residual reddish oil has so far not crystallized.

An identical product and percentage yield was obtained by the same procedure, starting with a mixture of 15 g. of *p*-methoxydibenzoylmethane, 15 g. of silver oxide, 100 cc. of ordinary acetone and 30 g. of methyl iodide. The filtered solution was evaporated, the oily residue dissolved in ether, the suspended silver iodide removed and the product finally isolated as above.

In either case the product tends to separate as an oil unless the solution is seeded just after the petroleum ether is added and if the growth of the crystals is hurried.

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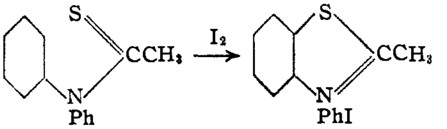
A Direct Synthesis of 2-Methylbenzothiazolium Salts[1]

BY L. G. S. BROOKER AND H. W. J. CRESSMAN

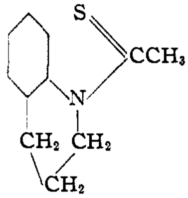
One of the simplest methods of preparing bases of the benzothiazole and naphthothiazole series is that devised by Jacobson,[2] which consists in the oxidation of the thioacetyl derivatives of primary aromatic amines in cold alkaline solution. Alkyl quaternary salts of these bases may be prepared by direct addition of alkyl iodides, *p*-toluenesulfonates, or the like.

It is not possible to attach simple aryl or certain other groups to the nitrogen atoms of benzothiazole bases in this way, however, and 2-methyl-3-phenylbenzothiazolium iodide (II) has been prepared by another route[3] which utilizes 3-phenyl-2(3)-benzothiazolone[4] as the starting material but which involves several steps.

Jacobson's alkaline oxidative method cannot be applied to the thioacetyl derivatives of secondary amines such as I, since such compounds are insoluble in alkali, but oxidation of I with iodine in aqueous acetic acid solution brought about the desired ring closure, and II was obtained in small yield as the triiodide, which gave the iodide on treatment with sulfur dioxide.[5]


I II

Starting with thioacetyltetrahydroquinoline (III), on the other hand, it was possible by this method to prepare the hitherto unknown 2-methyl-3,4-trimethylenebenzothiazolium iodide (IV) in moderately good yield. The 2-methyl group in this salt is very reactive, and the carbocyanine dye V, for example, was obtained quite smoothly using ethyl orthoformate. This dye is the higher vinylene homolog of a simple thiacyanine containing 3,4-trimethylene rings prepared by König, Kleist and Götze[6] from 3,4-trimethylene-2(3)-benzothiazolone. A number of other dyes have been prepared using IV.[5]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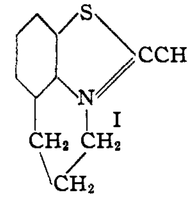
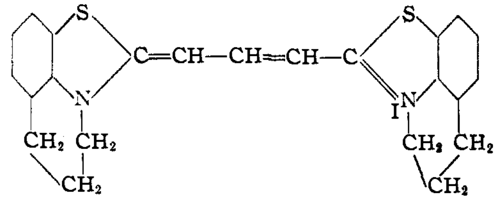

IV


V

Experimental

1-Thioacetyl-1,2,3,4-tetrahydroquinoline was prepared by heating 17.5 g. (1 mol) of 1-acetyl-1,2,3,4-tetrahydroquinoline with 11.1 g. (0.5 mol) of phosphorus pentasulfide in 30 cc. of dry pyridine to the refluxing point of the solvent for one half-hour with stirring. After allowing to cool, water precipitated an oily product that became crystalline on stirring with fresh portions of water. It separated from methyl alcohol in lustrous, almost colorless crystals with m. p. 68–70°; yield 70–74%.

Anal. Calcd. for $C_{11}H_{13}NS$: S, 16.77. Found: S, 16.62.

2-Methyl-3,4-trimethylenebenzothiazolium Iodide (IV) —In a typical experiment, 5.7 g. (1 mol) of 1-thioacetyl-1,2,3,4-tetrahydroquinoline was mixed with 15.2 g. (2 mols) of iodine, 2.5 g. (1 mol) of anhydrous sodium acetate, 4.5 g. (1 mol) of sodium iodide and 300 cc. of 50% acetic acid and the mixture boiled under reflux for one hour; triiodide (4.5 g., 26% yield) separated on cooling. This could be recrystallized from acetic acid in yellowish crystals with m. p. 121–123° dec.

Anal. Calcd. for $C_{11}H_{12}I_3NS$: I, 66.67. Found: I, 64.85.

The salt was reduced by bubbling sulfur dioxide through the hot suspension in absolute ethyl alcohol. The insoluble salt gradually dissolved, and the iodide separated on cooling; yield was almost quantitative. After a further crystallization from methyl alcohol, the almost colorless crystals had m. p. 254–256°.

Anal. Calcd. for $C_{11}H_{12}INS$: I, 40.03. Found: I, 40.24.

3,4,3',4'-Di-(trimethylene)-thiacarbocyanine Iodide (V). —One and one-tenth grams of IV (2 mols), 1 g. of ethyl orthoformate (1 mol plus 300% excess), and 30 cc. anhydrous pyridine were heated under reflux for forty-five

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[1] Communication No. 1009 from the Kodak Research Laboratories.

[2] Jacobson, *Ber.*, **19**, 1067 (1886).

[3] (a) Brooker and Williams, U. S. Patent 2,330,203; (b) Brooker, Keyes and Williams, THIS JOURNAL, **64**, 200 (1942).

[4] Passing, *J. prakt. Chem.*, **153**, 1 (1939).

[5] Brooker and Cressman, U. S. Patent 2,317,357.

[6] König, Kleist and Götze, *Ber.*, **64**, 1664 (1931).