benzenesulfonic acid; accordingly, since the *p*-(*p*-aminophenyl)-benzenesulfonamide prepared from this was identical with that obtained from *p*-aminobiphenyl, the structure of the latter was established.

***p*-(*p*-Nitrophenyl)-benzenesulfonyl Chloride.**—This compound was prepared by the method of Gabriel and Dambergis[2] and also by adding, with good stirring, *p*-nitrobiphenyl to two and one-half moles of chlorosulfonic acid at a temperature below 15°, then allowing the temperature to rise to that of the room and finally to 60° for two hours. The dark, sirupy liquid was then poured, with vigorous stirring, into a slush of ice. After filtering, pressing out on a porous plate and recrystallizing from acetic acid, the yellow crystals melted at 178°, the melting point given by Gabriel and Dambergis,[2] yield 94%.

***p*-(*p*-Aminophenyl)-benzenesulfonamide.**—To 10 g. of *p*-(*p*-nitrophenyl)-benzenesulfonamide[2] dissolved in 200 cc. of ethanol, were added 8 g. of tin and 50 cc. of concd. hydrochloric acid. After heating for one and one-half hours, the material was neutralized with sodium hydroxide, diluted to a volume of 600 cc. and acidified with 15 cc. of concd. hydrochloric acid. The tin sulfide precipitated by hydrogen sulfide was removed by filtration, the filtrate made alkaline with ammonium hydroxide and the product so obtained was purified by recrystallization from ethanol; m. p. 263° (cor.), unchanged when mixed with product prepared from *p*-aminobiphenyl, yield, 3.1 g.

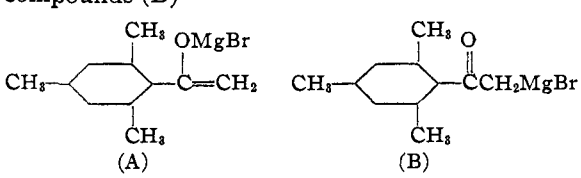
CHEMICAL LABORATORY
COLLEGE OF LIBERAL ARTS AND SCIENCES
TEMPLE UNIVERSITY
PHILADELPHIA, PENNSYLVANIA

RECEIVED DECEMBER 18, 1940

Metallic Derivatives of Acetomesitylene

BY HENRY GILMAN AND R. G. JONES

Bromomagnesium derivatives of sterically hindered ketones, like acetomesitylene, give enolates (A) which behave like true organomagnesium compounds (B)[1]



(A) (B)

In view of the extensive studies by Fuson and co-workers and Kohler and co-workers[1b] on the reaction of these bromomagnesium types with the carbonyl group, one might have predicted a positive Michler ketone color test.[2a] We have found that the bromomagnesium derivative of acetomesitylene does give this color test. The bromomagnesium compound was prepared from phenylmagnesium bromide and an excess of acetomesitylene. Phenylmagnesium bromide was selected in preference to an alkylmagnesium halide because the recently described[2b] Color Test III differentiates between reactive *aryl*metallic compounds and *alkyl*metallic types. In this manner, any uncertainty concerning the influence of phenylmagnesium bromide is ruled out, for the negative test with triphenylbismuth dichloride (Color Test III) showed the absence of phenylmagnesium bromide in the bromomagnesium compound prepared from it and acetomesitylene.

Of greater interest are the metallic derivatives prepared from RLi and RNa compounds. If acetomesitylene is an equilibrium mixture of the keto and enol forms, the more reactive organolithium[2c] and organosodium[2d] compounds might be expected to add appreciably to the carbonyl group. The large quantities of acetomesitylene recovered subsequent to hydrolysis belied any significant addition.[3] Furthermore, acetomesitylene with excess methyllithium evolved essentially the theoretical volume of methane.

Both the lithium and sodium derivatives of acetomesitylene gave a positive Michler ketone test. Unlike the bromomagnesium salt, the lithium compound is completely soluble in ether.

If a formula like (B) is correct for the lithium and sodium derivatives of acetomesitylene, it is not novel to find within a molecule a carbonyl group and a reactive C-M linkage for C-Li linkages have been prepared recently in molecules containing reactive anil and carbonyl groups.[4a] It is improbable that coördinate compounds are formed in the Michler ketone color tests with the lithium and sodium derivatives.[4b]

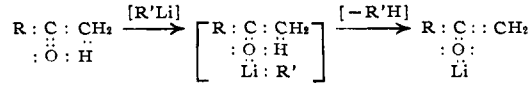
Experimental Part

Phenylmagnesium Bromide.—A solution of 4.87 g. (0.030 mole) of acetomesitylene in 25 cc. of ether was added to 10 cc. of 2.40 molar phenylmagnesium bromide. After refluxing for one hour the mixture was allowed to cool. Both the white crystalline solid and the clear supernatant

(1) (a) Malmgren, *Ber.*, **36**, 2608 (1903). (b) Fuson, Fugate and Fisher, THIS JOURNAL, **61**, 2362 (1939). This article contains references to earlier work, particularly by Kohler and co-workers and Fuson and co-workers.

(2) (a) Gilman and Schulze, *ibid.*, **47**, 2002 (1925). (b) Gilman and Yablunky, *ibid.*, **63**, 839 (1941). (c) Gilman and Kirby, *ibid.*, **55**, 1265 (1933). (d) Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

(3) It is possible that the lithium and sodium atoms first added to the oxygen of the carbonyl form; then the enolate developed with the accompanying formation of R'H, the hydrogen coming from the methyl group and the R' from the initial R'Li or R'Na compound



(4) (a) Gilman and Spatz, THIS JOURNAL, **62**, 446 (1940). (b) Gilman and Jones, *ibid.*, **62**, 1243 (1940).

ether gave positive Michler ketone tests. Tests with triphenylbismuth dichloride were negative.[2b]

Organolithium Compounds.—A solution of 8.2 g. (0.05 mole) of acetomesitylene in 25 cc. of ether was added dropwise to a refluxing ether solution of 0.061 mole of methyllithium. The evolved gas (methane by combustion) was 97% of the theoretical quantity. Hydrolysis of the clear ethereal solution yielded 85.5% of acetomesitylene. This experiment was checked.

From a related experiment using 8.0 g. (0.049 mole) of acetomesitylene and 0.10 mole of phenyllithium in 85 cc. of ether, there was recovered 7.8 g. or a 97% yield of acetomesitylene.

The lithium derivative prepared from 2.43 g. (0.015 mole) of acetomesitylene in 10 cc. of ether and 0.013 mole (15 cc. of 0.88 molar ether solution) of *n*-butyllithium or phenyllithium gave a weak but definite Michler ketone color test.

Phenylsodium.—To phenylsodium, prepared by stirring a mixture of 5.7 g. (0.25 g. atom) of sodium sand, 11.2 g. (0.10 mole) of chlorobenzene and 100 cc. of dry benzene for six hours at 35–40°, was added dropwise 24.3 g. (0.15 mole) of acetomesitylene in 25 cc. of benzene. The reaction was highly exothermic. After standing for twelve hours, samples gave good positive tests with Michler ketone. Hydrolysis, by the cautious addition of water, gave 20.9 g. or an 86% yield of acetomesitylene. No other identifiable products were isolated.

CHEMICAL LABORATORIES
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED JANUARY 13, 1941

The Antioxidant Properties of Antihemorrhagic Compounds

BY CALVIN GOLUMBIC

Many quinols possess the property of delaying the oxidative deterioration of fats and oils.[1,2,3] The antioxygenic capacity of the corresponding quinones is less than that of the quinols. However, the widespread occurrence of quinones in nature and the presence of vitamin K in alfalfa[4] and in soybean oil[5] prompted an investigation of the antioxygenic properties of these compounds,[6] particularly of those exhibiting vitamin K activity. The oxygen absorption method[7] was used to measure the induction period of the substrates with and without added stabilizers; lard, the ethyl esters of lard fatty acids, and purified fatty acids were used.

Effective antioxidants are found among the antihemorrhagic α-naphthols, α-naphthoquinones and *p*-benzoquinones and corresponding quinols (Table I). α-Naphthol and its homologs are by far the most active. The methyl α-naphthols are less effective than the parent compound and their action varies with the position of the methyl substituent. Similarly, the 2-methyl homolog of α-naphthohydroquinone exhibits diminished antioxygenic activity and the corresponding quinone, 2-methyl-1,4-naphthoquinone, is inactive. Similar relations between structure and antioxygenic activity have previously been observed in the benzene series.[2,3] Duroquinone and α-tocoquinone, reported to show slight vitamin K activity,[8,9] do not stabilize lard.[3]

TABLE I

THE ANTIOXYGENIC ACTION OF NAPHTHOLS, QUINONES AND QUINOLS ON LARD AND ON ETHYL ESTERS OF LARD FATTY ACIDS

Substrate	% Inhibitor added	Antioxygenic index at 75°[a]
Ethyl esters of lard fatty acids	0.02 α-naphthol	30
	.02 2-methyl-1-naphthol	24
	.02 3-methyl-1-naphthol	16
Lard	.10 α-naphthoquinone	1.5
	.04 α-naphthohydroquinone	7
	.10 2-methyl-1,4-naphthohydroquinone	1.5
Lard	.10 *p*-xyloquinone	1.5
	.04 *p*-xylohydroquinone	5
Lard	.02 β-naphthoquinone	8
	.10 β-lapachone	2.5
	.02 dehydro-iso-β-lapachone	2
	.02 pyrano-*o*-quinone (from α-tocopherol)	2

[a] The antioxygenic index is the ratio of the induction period in hours of the protected fat to that of the unprotected.

The effectiveness of benzenoid inhibitors is increased by the presence of additional hydroxyl groups[1]; this effect was not observed among the naphthenoid compounds. Thus, phthiocol and its corresponding quinol are not stabilizers. Other 2,3-disubstituted α-naphthoquinones, lomatiol, lapachol and the cyclic derivatives, α-lapachone and isopropylfuran α-naphthoquinone, are also inactive under the conditions used.

(1) H. A. Mattill, *J. Biol. Chem.*, **90**, 141 (1931).
(2) H. S. Olcott, THIS JOURNAL, **56**, 2492 (1934).
(3) C. Golumbic, *ibid.*, **63**, 1143 (1941).
(4) S. B. Binkley, D. W. MacCorquodale, S. A. Thayer and E. A. Doisy, *J. Biol. Chem.*, **130**, 219 (1939).
(5) H. J. Almquist and A. A. Klose, THIS JOURNAL, **61**, 1610 (1939).
(6) Grateful acknowledgment is extended to Dr. L. F. Fieser, Harvard University, for generous samples of lomatiol, lapachol and their cyclic derivatives. Samples of the methyl α-naphthols were kindly furnished by Dr. M. Tishler, Merck and Company, Rahway, N. J.
(7) R. B. French, H. S. Olcott and H. A. Mattill, *Ind. Eng. Chem.*, **27**, 724 (1935).
(8) R. Kuhn, K. Wallenfels, F. Weygand, Th. Moll and L. Hepding, *Naturwissenschaften*, **27**, 518 (1939).
(9) H. Dam, J. Glavind and P. Karrer, *Helv. Chim. Acta*, **23**, 224 (1940).