reaching from the end of a primary molecule to the first cross-linkage along its length are not permanently distorted by a deformation of the sample. The latter, therefore, generally will not undergo crystallization, but rather will act like diluents dispersed in the oriented portion of the network

Equation (6) can be deduced as a special case of the more general dependence stated in *italics* above. If the concentration of cross-linkages (degree of vulcanization) is fixed, the percentage of the rubber occurring in non-orienting terminal chains will be inversely proportional to M, the molecular weight of the primary molecules (*i. e.*, the molecular weight of the rubber molecules before vulcanization). Hence, in accordance with the above generalization, the tensile strength varies linearly with $1/M$ at constant degree of cross-linking.

This interpretation of the tensile strength-molecular weight relationship cannot be applied to cellulose acetate which has no primary valence network. It would appear that the similar dependence on molecular weight in this case is to be regarded as coincidental rather than as an indication of identical structural behavior when subjected to severe stresses. In this connection Spurlin[3] has suggested that rupture originates at the ends of molecules and, hence, that the ease of failure (conversely the strength) should depend on the *number* of ends of molecules. This will explain the explicit dependence of strength on the number average molecular weight; it does not seem to offer a satisfactory basis for *linear* dependence on $1/M$, or $1/\overline{M}_n$, however.

(3) H. M. Spurlin, "Cellulose and Cellulose Derivatives," edited by Emil Ott, Interscience Publishers, Inc., New York, N. Y., 1943, pp. 9, 935–936.

RESEARCH LABORATORY
GOODYEAR TIRE AND RUBBER COMPANY
AKRON, OHIO
RECEIVED AUGUST 28, 1945

Reaction of Chloromethyl Ether with Ethyl Acetoacetate in the Presence of Boron Trifluoride[1]

BY ROBERT LEVINE AND CHARLES R. HAUSER

It has been shown in this Laboratory[2] that, in the presence of boron trifluoride, certain ethers and alcohols alkylate acetoacetic ester to form the corresponding C-alkyl derivative. It has now been found that, under similar conditions, chloromethyl ether reacts with acetoacetic ester to form methylenediacetoacetic ester (III). The reaction involves presumably the chloromethylation of acetoacetic ester to form the C-alkyl derivative (I). This intermediate then either alkylates unchanged acetoacetic ester to form (III) or loses hydrogen chloride to form (II) which undergoes a Michael condensation with unchanged acetoacetic ester to form (III).

$CH_3COCHCO_2C_2H_5$ (with CH_2Cl on the CH) — I

$CH_3COCCO_2C_2H_5$ (with $=CH_2$ on the C) — II

$CH_3COCHCO_2C_2H_5$ / CH_2 / $CH_3COCHCO_2C_2H_5$ — III

The chloromethylation with boron trifluoride to form the C-alkyl derivative is in contrast to the reaction of chloromethyl ether with sodium acetoacetic ester which forms mainly the O-methoxymethyl derivative,[3] $CH_3C(OCH_2OCH_3)=CHCO_2C_2H_5$.

Procedure.—A mixture of one or one-half mole of chloromethyl ether and one-half mole of ethyl acetoacetate was saturated with boron trifluoride at 0° as described previously[2] for alkylation with ordinary alcohols and ethers. After the reaction mixture had come to room temperature, it was poured into aqueous sodium acetate. The mixture was extracted with ether and the dried ethereal extract distilled. There was obtained a 33% yield of methylene-diacetoacetic ester, b. p. 192–210° at 20 mm. with decomposition,[4] giving, with ferric chloride solution, a deep purple enol test, and with alcoholic ammonia, ethyl dihydrolutidinedicarboxylate, m. p. 174–176°.[4] A non-distillable viscous residue (10–13 g.) remained in the distilling flask.

(3) Simonsen and Storey, *J. Chem. Soc.*, **95**, 2108 (1909).
(4) Knoevenagel, *Ann.*, **281**, 94 (1894).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, N. C.
RECEIVED SEPTEMBER 17, 1945

(1) Paper XXXI on "Condensations"; paper XXX, THIS JOURNAL, **67**, 1510 (1945).
(2) Adams, Abramovitch and Hauser, *ibid.*, **65**, 552 (1943).

Determination of Pyrrole

BY F. FROMM[1]

A photometric micromethod for the determination of pyrrole has been based on the blue color produced in the reaction between pyrrole and isa-

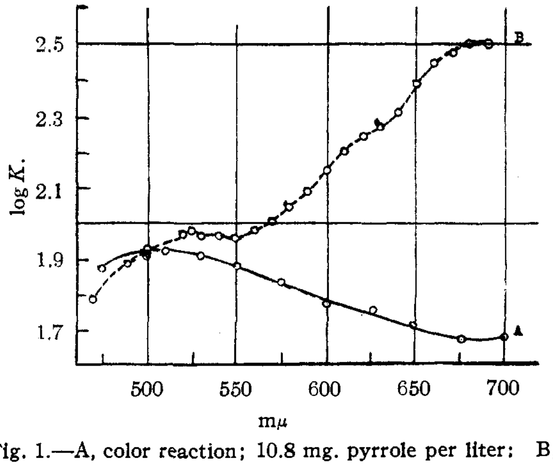


Fig. 1.—A, color reaction; 10.8 mg. pyrrole per liter; B, pyrrole blue B; 5.3 mg. pyrrole per liter.

tin in boiling acid solution.[1] It was assumed that this coloration was due to the formation of β-(5-pyrrolenyl)-isatin or pyrrole blue B. Recently it has been shown,[2] however, that pyrrole blue B in glacial acetic acid has a maximum absorption at 680–690 mμ while the maximum absorption in the microreaction was observed in the range for 510–560 mμ. For a more exact comparison the absorption spectrum of the color reaction was determined in a Hilger–Nutting spectrophotometer. The resulting curve A in Fig. 1 is quite different from the spectrum of pyrrole blue B, shown in curve B. The logarithm of specific extinction K is calculated per grams of pyrrole per liter. Thus the compound formed in the color reaction is certainly not pyrrole blue B but seems to be its decomposition product which also forms when solutions of pyrrole blue B are standing for some time. It has been indicated[2] that the decomposition product has an absorption maximum at 520 mμ.

The author is greatly indebted to the Chemistry Department of the University of Michigan for the permission to use a spectrophotometer and to Dr. F. F. Blicke for the supply of pyrrole.

(1) F. Fromm, *Mikrochemie*, **17**, 141 (1935).
(2) F. Fromm, THIS JOURNAL, **66**, 1227 (1944).

COLEGIO DEL SAGRADO CORAZÓN
SANTURCE, PUERTO RICO RECEIVED AUGUST 21, 1945

Benzophenone-ascorbic Acid

BY PHILIPPOS E. PAPADAKIS

In view of the known bacteriological action of benzophenone in human tubercle bacilli *in vitro*[1] the following benzophenone derivative of ascorbic acid is reported.[2]

Procedure.—Equivalent quantities of ascorbic acid and benzophenone chloride in dry toluene were heated under a reflux condenser until no more hydrogen chloride was coming off. The oil-bath temperature was 90°. After filtering, the residue was treated with ice water to dissolve any unreacted ascorbic acid, then with benzene to remove any benzophenone formed and finally it was recrystallized from methyl alcohol; m. p. 207–208°. The substance is insoluble in water, soluble in methyl alcohol and ether. Further work is contemplated for the elucidation of the structure of this substance.

Anal. Calcd. for $C_{19}H_{16}O_6$: C, 67.03, H, 4.73. Found: C, 67.04, H, 4.9.

The microanalyses were done by D. Rigakos of the Rockefeller Institute for Medical Research.

Acknowledgment.—The author wishes to express his appreciation and thanks to Dean Charles M. McConn of Washington Square College, to Professor Arthur C. DeGraff and to Dr. Robert Lehman of the Department of Therapeutics for the arrangement which made it possible for him to do this work.

(1) B. L. Freedlander, *Am. Rev. Tuberc.*, **49**, 543 (1944).
(2) This work was completed in 1942.

DEPARTMENT OF THERAPEUTICS
NEW YORK UNIVERSITY
COLLEGE OF MEDICINE
NEW YORK 16, N. Y. RECEIVED JULY 17, 1945

The Decomposition of Phenyliodoso Acetate[1]

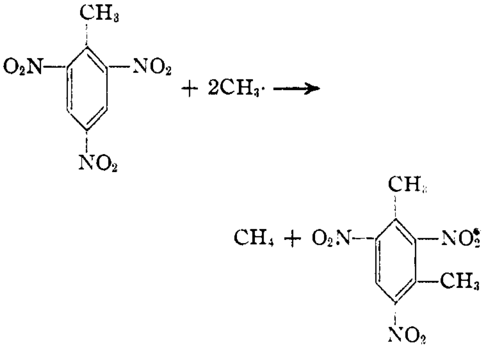
BY REUBEN B. SANDIN AND WILLIAM B. MCCORMACK

Fieser and co-workers[2] have carried out some very interesting work on the alkylation of α-naphthoquinones and aromatic nitro compounds with tetravalent lead esters, such as lead tetraacetate. By this method, for example, they were able to convert trinitrotoluene in yields as high as 32% into trinitro-*m*-xylene. Because of the similarity between iodoso compounds and certain compounds of lead,[3] it occurred to the authors of this paper that phenyliodoso acetate, like lead tetraacetate, might act as a methylating agent. It has already been shown by Criegee and Beucker[4] that aryliodoso acetates, like lead tetraacetate, can oxidize unsaturated compounds and can bring about the fission of α,β-glycols.

The experimental work described in this paper indicates that phenyliodoso acetate can behave as a methylating agent. By means of phenyliodoso acetate, trinitrotoluene has been converted into trinitro-*m*-xylene to an extent of about 20%. It has also been shown that when phenyliodoso acetate is heated by itself, decomposition occurs above 160°, and some of the reaction products are phenyl iodide, carbon dioxide, ethane and methane. We believe that the following equations represent the sequence of events[5]

$$C_6H_5I(OCOCH_3)_2 \longrightarrow C_6H_5I + 2CH_3COO\cdot \quad (I)$$

$$2CH_3COO\cdot \longrightarrow 2CH_3\cdot + 2CO_2 \quad (II)$$



(III)

Also, the thermal decomposition of some of the phenyliodoso acetate appears to follow reactions I and II. This is followed by the union of methyl

(1) Originally received May 7, 1945.
(2) Fieser and Chang, THIS JOURNAL, **64**, 2043 (1942); Fieser, Clapp and Daudt, *ibid.*, **64**, 2052 (1942); Fieser and Oxford, *ibid.*, **64**, 2060 (1942).
(3) Sandin, *Chem. Rev.*, **32**, 258 (1943).
(4) Criegee and Beucker, *Ann.*, **541**, 218 (1939).
(5) The Referee has very kindly suggested this reaction mechanism.