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 $1/\bar{M}_n$, however.

---

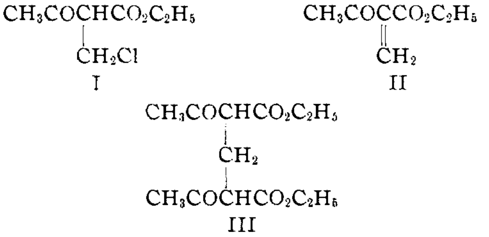
[3] H. M. Spurlin, "Cellulose and Cellulose Derivatives," edited by Emil Ott, Interscience Publishers, Inc., New York, N. Y., 1943, pp. 9, 935–936.

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).


$$\underset{\text{I}}{CH_3CO\underset{CH_2Cl}{\underset{|}{C}}HCO_2C_2H_5} \qquad \underset{\text{II}}{CH_3CO\underset{CH_2}{\underset{\|}{C}}CO_2C_2H_5}$$
$$\underset{\text{III}}{\begin{array}{c} CH_3COCHCO_2C_2H_5 \\ | \\ CH_2 \\ | \\ CH_3COCHCO_2C_2H_5 \end{array}}$$

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] $CH_3\underset{OCH_2OCH_3}{\underset{|}{C}}{=}CHCO_2C_2H_5$.

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.

---

[1] Paper XXXI on "Condensations"; paper XXX, THIS JOURNAL, **67**, 1510 (1945).

[2] Adams, Abramovitch and Hauser, *ibid.*, **65**, 552 (1943).

[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

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-

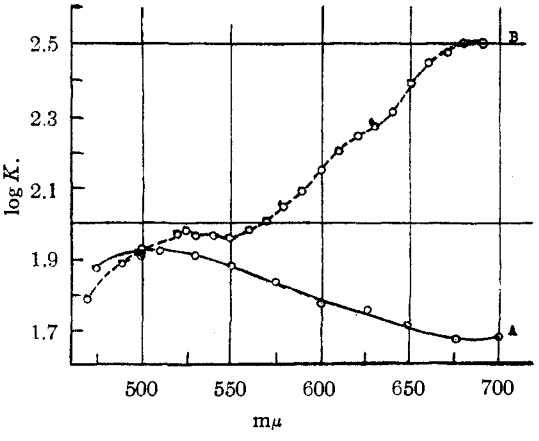


Fig. 1.—A, color reaction; 10.8 mg. pyrrole per liter; B, pyrrole blue B; 5.3 mg. pyrrole per liter.