

chloroethane, has made a sensitive colorimetric test essential for its detection and determination in such fields of study as spray residues, pharmacology, solubility in water, and vapor pressure. We wish to report the development of a very sensitive color test for this and related compounds based on nitration to polynitro derivatives and the production of intense colors upon addition of methanolic sodium methylate to a benzene solution of the nitration products.

Several pure chromogenic compounds were prepared by nitration with concentrated sulfuric acid-fuming nitric acid (1:1 by volume) at 100° for 1 hour and recrystallization from acetone-ethanol: Tetranitro-*p,p'*-DDT, or 2,2-bis-(4-chloro-3,5-dinitrophenyl)-1,1,1-trichloroethane, m. p. 223.5–224.5° (cor.). *Anal.* Calcd. for C<sub>14</sub>H<sub>5</sub>Cl<sub>5</sub>N<sub>4</sub>O<sub>8</sub>: C, 31.46; H, 0.94. Found: C, 31.66; H 1.07.<sup>2</sup> Nitration products of DDD, or 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane, and of the ortho, para isomer of DDT, or 2-*o*-chlorophenyl-2-*p*-chlorophenyl-1,1,1-trichloroethane, prepared in the same manner, m. p. 224.5–225.5° (cor.) and 229.5–230° (cor.), respectively.

Spectrophotometric curves were obtained<sup>3</sup> in the range 400–750 m $\mu$  on a mixture of one volume of a benzene solution of each of the nitrated compounds with two volumes of sodium methylate reagent (5.0 g. sodium per 100 ml. methanol solution) at a final concentration of 0.020 g. of compound per liter. A General Electric recording spectrophotometer was used with 1-cm. absorption cells. Data taken from the curves are given in Table I.

TABLE I  
SPECTROPHOTOMETRIC DATA

Nitrated derivative from	Wave length m $\mu$	Specific extinction 1.liters/g./cm.
<i>p,p'</i> -DDT	600 max.	48.0
	443 min.	5.9
<i>p,p'</i> -DDD	598 max.	38.7
	442 min.	4.7
<i>o,p'</i> -DDT	590 max.	25.0
	558 min.	22.7
	511 max.	27.8
	426 min.	5.6

The curves were obtained within 10 minutes after adding the reagent to minimize the effect of the slow fading of the colors. The derivatives of *p,p'*-DDT and *p,p'*-DDD give blue colors with one absorption maximum and one minimum in the range studied, while the derivative of the ortho, para isomer of DDT gives a violet red color with two maxima and two minima.

The spectrophotometric curves indicate the feasibility of determining both the total and relative amounts of *p,p'*-DDT and *o,p'*-DDT in mixtures of the two, and the high extinction

(2) Analysis by W. F. Barthel.

(3) Grateful acknowledgment is made to Sylvan H. Newberger, of the U. S. Food and Drug Administration, for cooperation in securing the spectrophotometric data.

values obtained illustrate the sensitivity that can be expected in the detection of DDT. While a number of interferences have been found, some would not be expected to occur or be used with DDT; others can be removed or detected in some manner. A colorimetric analytical method for the determination of DDT making use of these reactions has been developed, and a description is being prepared.

The chemical reactions of these polynitro compounds and the nitration of degradation products of DDT (such as the dehydrochlorinated derivative) are being further investigated. More complete spectrophotometric data and a theory which accounts for the colors and absorption spectra produced by sodium methylate will be elaborated upon in forthcoming papers.

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#### THE STRUCTURE OF ETHYL $\beta$ -IONYLIDENEACETATE<sup>1</sup>

Sir:

Since ethyl  $\beta$ -ionylideneacetate, prepared from  $\beta$ -ionone by the Reformatsky reaction, is an important intermediate in the synthesis of compounds related to vitamin A, its " $\beta$ " structure must be definitely established. The " $\beta$ " structure proposed by Karrer, *et al.*,<sup>2</sup> has been questioned recently by Sobotka and co-workers<sup>3</sup> on the basis of pyrolysis and absorption spectra studies.

These workers obtained  $\alpha$ -ionone by heating the barium salt derived from the ester obtained from the Reformatsky reaction on  $\beta$ -ionone, indicating that rearrangement from  $\beta$  to  $\alpha$  form had occurred during either the Reformatsky reaction or the heat treatment of the barium salt. Since the absorption spectrum of the ethyl  $\beta$ -ionylideneacetate does not conform to that anticipated for a compound containing three olefin bonds conjugated with a carbethoxy group, they have concluded that a rearrangement from  $\beta$  to  $\alpha$  structure occurs during the Reformatsky reaction. They believe that stereoisomerism accounts for the differences in the products prepared from the  $\alpha$ - and  $\beta$ -ionones.

Recent work in this laboratory<sup>4</sup> on the ionylideneacetones prepared from the ionylideneacetates and cyanoacetates seems to justify the assignment of the " $\beta$ " structure to the ester obtained from  $\beta$ -ionone. We have now obtained additional evidence for the " $\beta$ " structure from ozonolysis of the ester in question. In duplicate

(1) This work was made possible by a research grant from Sharp and Dohme, Inc.

(2) Karrer, Salomon, Morf and Walker, *Helv. Chim. Acta*, **15**, 878 (1932).

(3) (a) Sobotka, Bloch and Glick, *THIS JOURNAL*, **65**, 1961 (1943); (b) Sobotka and Bloch, *Chem. Rev.*, **34**, 435 (1944).

(4) Young, Andrews and Cristol, *THIS JOURNAL*, **66**, 520 (1944).

experiments only geronic acid semicarbazone could be isolated.<sup>5</sup> It is unlikely that this acid is formed from rearrangement of the  $\alpha$ -form during ozonization since  $\alpha$ -ionone,  $\alpha$ -ionylideneacetone, and the ethyl ionylideneacetate from  $\alpha$ -ionone all give only isogeronic acid. In view of the fact that the  $\beta$  ester in question gives only geronic acid and the  $\alpha$  ester gives only isogeronic acid while an equimolar mixture of these two esters gives a mixture of geronic and isogeronic acids, it is difficult for us to assign the same ( $\alpha$ ) structure to both esters. Although the yields of isogeronic and geronic acids obtained from the esters in this preliminary study were only 13–19%, they were consistent with those we obtained on the  $\alpha$ - and  $\beta$ -ionones of known structure.

Further work on ozonization and polarographic studies of the ethyl  $\alpha$ - and  $\beta$ -ionylideneacetates is in progress in order to establish unequivocally the structure of these substances.

Correction: In our previous publication, *THIS JOURNAL*, 66, 521 (1944), the data for the solid and liquid forms of  $\beta$ -ionylideneacetic acid are reversed in Table I. These items should read:

	$\lambda$ max. m $\mu$	$\epsilon$ max. b
$\beta$ -ionylideneacetic acid (solid) <sup>c</sup>	294, 260	13700, 12900
(liquid)	283	17700

(<sup>5</sup>) Karrer, Morf and Walker, *Helv. Chim. Acta*, 16, 975 (1933).

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#### THE REACTION OF BUTENYLMAGNESIUM BROMIDE WITH ACETOMESITYLENE

Sir:

In a study of the nature of the butenyl Grignard reagent it appeared that valuable information might be obtained from the composition of the butenes resulting from the enolization of ke-

tones by butenylmagnesium bromide. Acetomesitylene was chosen for this experiment as several investigators<sup>1a,b,c</sup> have shown that organometallic compounds such as ethylmagnesium bromide, *n*-butyllithium and phenylsodium do not add to the carbonyl group of this compound but give enolization products exclusively.

Contrary to expectation, the reaction of butenylmagnesium bromide with acetomesitylene gave virtually no enolization products. Less than 3% of the calculated amount of butene was detected. From the reaction mixture was recovered less than 12% of the original ketone and the principal product was a compound which we believe to be *s*-butenylmesitylmethylcarbinol (I); b. p. 119–123° (2 mm.),  $n_D^{20}$  1.5330; mol. wt. by hydrogenation, 214 (calcd. for C<sub>15</sub>H<sub>22</sub>O, 218); yield, 83%.

*Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>O: C, 82.54; H, 10.16. Found: C, 82.36; H, 10.23.

On distillation at atmospheric pressure, I cleaved smoothly to give butene and acetomesitylene. The latter compound was characterized by two derivatives. Ozonization of I gave formaldehyde, propionaldehyde and, apparently, acetomesitylene.

Benzylmagnesium chloride reacts with acetomesitylene to give benzylmesitylmethylcarbinol (II) in 52% yield. Enolization products amounted to 38%. The structure of II was established by oxidative degradation which gave benzoic acid. On strong heating, II did not cleave, but appeared to dehydrate.

Further studies of the addition of  $\beta$ , $\gamma$ -unsaturated Grignard reagents and other organometallic compounds are in progress.

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(1) (a) Kohler and Baltzly, *THIS JOURNAL*, 54, 4015 (1932); (b) Kohler, Jacobs and Sonnichsen, *ibid.*, 62, 785 (1940); (c) Gilman and Jones, *ibid.*, 63, 1162 (1941).

## NEW BOOKS

**Fundamentals of Chemistry and Applications.** By CHARLOTTE A. FRANCIS, A.M., Formerly Instructor in Chemistry, Teachers College, Columbia University, and EDNA C. MORSE, R.N., A.M., Instructor in Chemistry, Teachers College, Columbia University. Second edition. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1943. xi + 537 pp. 98 figs. 15 × 22 cm. Price, \$3.50.

Relatively few college teachers of elementary chemistry realize how the "other half lives," and learns, until they have read carefully a text such as this, planned and written for students in nursing and similar schools. The time allotted to a student nurse's course is short, for study, class and laboratory, and she is expected to understand and retain a considerable amount of descriptive general, inorganic and organic chemistry, much of it of course by brute force

memory. The field covered is limited by time and rather closely prescribed by hospital practice and the "Curriculum Guide for Schools of Nursing"; the instruction usually is by members of the hospital staff, often trained previously in the same school.

This book comprises thirty-one chapters, the first nineteen (280 pages) dealing with: Substances, Mixtures, Physical and Chemical Change, Compounds, Elements, Oxygen, Catalytic Agents, Combustion, Energy Transformations, Chemical Measurements, Chemical Shorthand, Bases-Acids-Salts-Radicals, Valence, Within the Atoms, Water, Reactions of Acids, Bases and Salts, Solutions-Colloids-Emulsions, Electrolytes and Ionization, Weak Electrolytes-Equilibrium-Water, Oxidation-Reduction. The remainder takes up Organic Chemistry, twelve chapters (235 pages) on: Introduction, Hydrocarbons and