

agitated by 18-inch propellers running at 270 r. p. m., and aerated at the rate of 200 liters per minute. The medium used contained 4% corn steep liquor solids, 4% lactose, and 1% calcium carbonate.

It will be seen that although shake flask yields varied considerably in every experiment, both Q176 and Q176A8 surpassed X-1612. In the tank tests Q176 gave yields higher than those thus far obtained with any other culture. Q176A8, however, failed to surpass X-1612.

The fundamental studies on variability in *Penicillium notatum* and *P. chrysogenum* of which these strains were a by-product will be reported in detail elsewhere. Upon request, transfers of any of the cultures mentioned in this note will be sent to laboratories engaged in penicillin research or production.

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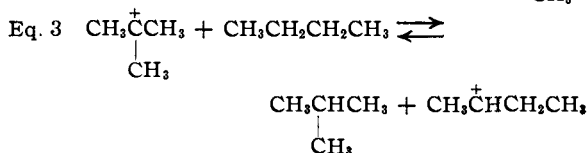
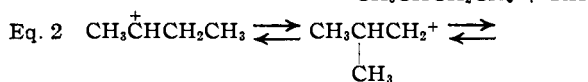
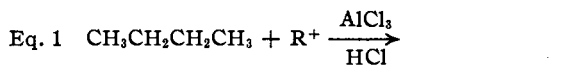
M. P. BACKUS<sup>1</sup>  
J. F. STAUFFER  
M. J. JOHNSON

RECEIVED DECEMBER 7, 1945

(1) With the assistance of O. H. Calvert, Eugene Dulaney, J. J. Stefaniak, F. B. Gailey and F. G. Jarvis.

### THE MECHANISM OF PARAFFIN ISOMERIZATION Sir:

It has been shown<sup>1</sup> that under controlled conditions paraffin hydrocarbons do not undergo isomerization in the presence of aluminum halide catalysts unless traces of olefins or their equivalent are present. These results suggest that the isomerization may proceed by a chain mechanism similar to that proposed<sup>2</sup> for the alkylation of isoparaffins with olefins. Thus, it is postulated that isomerization of *n*-butane proceeds by a sequence of reactions which may be expressed as follows in terms of carbonium ions<sup>3</sup> as has been done<sup>4</sup> in the case of alkylation mechanism.



(1) H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, in press (1946).

(2) L. Schmerling, *ibid.*, **66**, 1422 (1944).

(3) In accordance with current theory, carbonium ions are used in this paper as the active equivalent of alkyl halides or of olefins,<sup>5</sup> plus hydrogen halide.

(4) P. D. Bartlett, F. E. Condon and A. Schneider, *THIS JOURNAL*, **66**, 1531 (1944).

The reaction of Eq. 1 serves only to initiate the chain and the reactant, R<sup>+</sup>, need therefore be present in small amount only. The chain initiating ion, R<sup>+</sup>, may be produced in several ways. It may be formed by the addition of hydrogen chloride or hydrogen aluminum tetrachloride (HAlCl<sub>4</sub>, probably the true catalyst) to an olefin which is present in the paraffin as an impurity, or which is added as such, or which results from cracking of the paraffin. It may also be introduced in the form of an alkyl halide.

Dehydrogenation of the paraffin by reaction with the hydrogen chloride or hydrogen aluminum tetrachloride offers yet another means of obtaining the necessary chain-initiating ion:



Experimental evidence in support of this reaction may be found in the observation that minor quantities of hydrogen are actually formed during the initial stages of butane isomerization with a supported aluminum chloride catalyst and hydrogen chloride.<sup>5</sup> The rearrangement of the *s*-butyl-carbonium ion (Eq. 2) finds analogy in the rearrangement of olefins in the presence of acidic substances.<sup>6</sup> The reaction of Eq. 3 (as well as that of Eq. 1) is similar to the hydrogen-halogen exchange reaction which occurs when isoparaffins are contacted with *s*- or *t*-alkyl chlorides in the presence of aluminum chloride.<sup>3</sup>

In accordance with the lesser tendency of normal paraffins to undergo the exchange reaction, higher temperature or otherwise more severe reaction conditions are necessary for isomerization of normal paraffins than are required for the alkylation of isoparaffins.

It is evident that the mechanism herein proposed is also applicable to the isomerization of cycloparaffins.

(5) H. S. Bloch, unpublished results.

(6) F. C. Whitmore, *THIS JOURNAL*, **54**, 3274 (1932). See also Egloff, Hulla and Komarewsky "Isomerization of Pure Hydrocarbons," Reinhold Pub. Corp., New York, N. Y., 1942, Chap. II.

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(7) Original manuscript received June 7, 1945.

### LIGHT-FIELD ULTRAMICROPHOTOGRAPHY OF LYOGELS

Sir:

In a recent publication (*Ind. Eng. Chem.*, **37**, 786 (1945)) we reported on a new microscopic technique with ultra-illumination by incident light resulting in a dark-field effect, which has proved to be of particular value in the study of lyogels.

Since then we have made a great number of color microphotographs of such preparations, using Kodachrome A film. Due to the absence of any grain in the developed film, the color photographs lend themselves very well to considerable

enlargement. However, enlarged color prints can so far not be made by the individual, and reproduction of color pictures for periodicals or books is expensive.

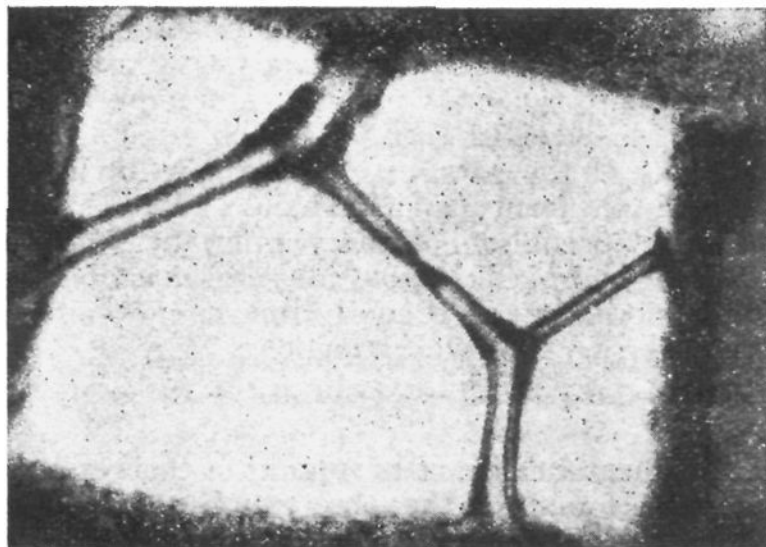


Fig. 1.—GR-S Rubber milled ten minutes, dissolved in benzene. Enlarged print from Kodachrome A film. Magnification is approx. 5000.

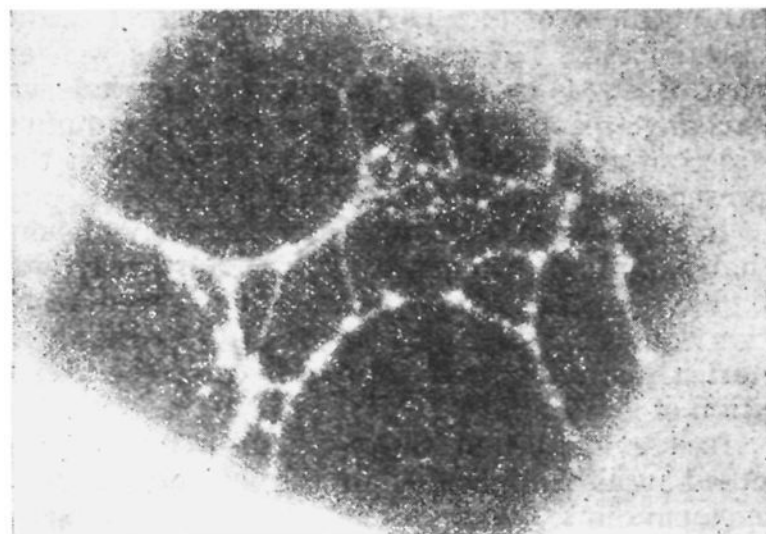


Fig. 2.—Pale crepe milled thirty minutes, dissolved in benzene. Ultra-illumination by incident light. Magnification is approx. 5000.

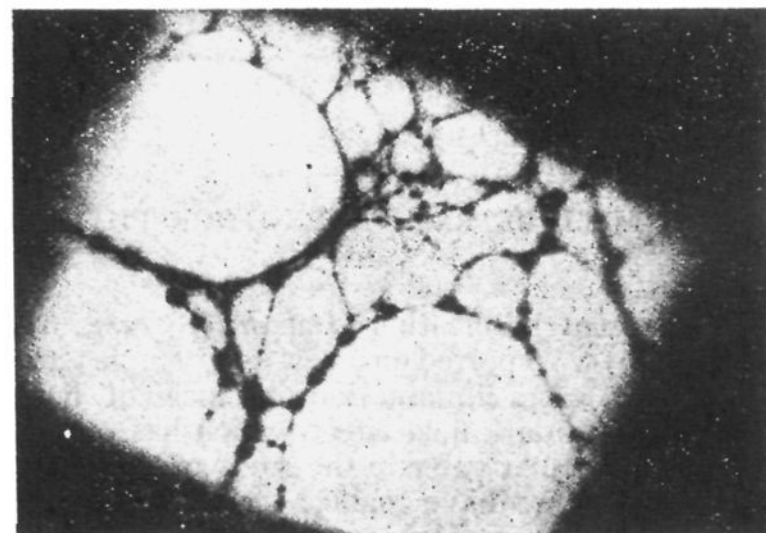


Fig. 3.—Pale crepe milled thirty minutes, dissolved in benzene. Print from positive film. Magnification is approx. 5000.

Since color photographs are definitely superior to regular black and white film for recording fine microstructures, we made enlargements on regular printing paper using the Kodachrome picture as negative. We have termed the so produced positive "light-field ultramicrophotograph," because the result is really a reversed ultramicroscopic effect. Wherever a specific color of the preparation is not the predominant factor in its study, this technique enables one to obtain very satisfactory prints from the color slide. Besides this, the light background generally offers a better contrast.

If no Kodachrome is available or desired and one still wants to benefit by this technique, one can expose the dark-field negative to a film and produce a positive which, if then used for making prints, will again give a light-field background.

The microphotographs are offered as illustrations.

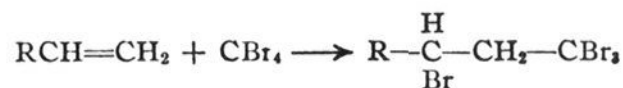
DEPARTMENT OF CHEMICAL ENGINEERING  
MASSACHUSETTS INST. OF TECH. ERNST A. HAUSER  
CAMBRIDGE 39, MASS. DESIREE S. LE BEAU

RECEIVED DECEMBER 12, 1945

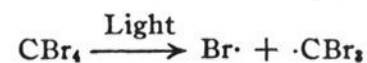
#### ADDITION OF CARBON TETRABROMIDE AND BROMOFORM TO OLEFINS

Sir:

When a mixture of an olefin and carbon tetrabromide is heated at 70–90° in the presence of 1–5 mole per cent. of a diacyl peroxide, the carbon tetrabromide adds to the olefin.



The mechanism of this type of addition has been discussed in previous papers.<sup>1</sup> However, carbon tetrabromide differs from the halides there mentioned in that its addition is initiated not only by diacyl peroxides but by visible light.



For example, a mixture of octene-1 (56 g.) and carbon tetrabromide (600 g.) was heated to 75° for seven hours in an apparatus illuminated internally by a mercury-filled coil coated with a fluorescent material so that it gave a white light.<sup>2</sup> Distillation of the reaction mixture yielded a product (196 g. = 88% on the basis of the octene-1 used) which boiled at 127° (0.02 mm.). The substance was 1,1,1,3-tetrabromo-*n*-nonane ( $n_D^{20}$  1.5488).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{16}\text{Br}_4$ : Br, 72.1; mol. wt., 444. Found: Br, 72.8; mol. wt., 441.

Excellent yields of the same substance were also obtained when a similar mixture of octene-1 and carbon tetrabromide was heated to 80° in the pres-

(1) Kharasch, Jensen and Urry, *Science*, **102**, 128 (1945); Kharasch, Urry and Jensen, *THIS JOURNAL*, **67**, 1626 (1945); Kharasch, Jensen and Urry, *ibid.*, **67**, 1864 (1945).

(2) Carbon tetrachloride, phosphorus trichloride and a number of other substances add to olefins when mixtures of olefins with these halides are exposed to ultraviolet light.