suspensions were dissimilar only in the region from 8 to 12 microns, possibly due to the differences in crystal structure.

Biological assays of the two forms showed no significant difference in estrogenic activity.[3]

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(3) Modified Kahut-Doisy method, by S. Margolin and M. T. Spoerlein, Biological Laboratories of this Company.

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Isomerization of Saturated Hydrocarbons. VIII.[1] The Effect of Oxygen and Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF

The promoting effect of oxygen upon the isomerization of *n*-butane and *n*-pentane in the presence of either aluminum chloride or aluminum bromide has been reported previously.[3] This study has now been extended to determine whether oxygen in the presence of aluminum bromide but in the absence of added hydrogen bromide promotes the isomerization of saturated cyclic hydrocarbons such as methylcyclopentane to cyclohexane. The experiments were conducted in either quartz or Pyrex reaction tubes.

It was noticed that in diffused light, and a Pyrex reaction tube, with methylcyclopentane, aluminum bromide and oxygen in a molal ratio of 100:2:0.2, isomerization of methylcyclopentane to cyclohexane does not occur. When the reaction tube was exposed for eighteen hours to a quartz cadmium-mercury arc lamp 6% of the methylcyclopentane was isomerized; the extent of isomerization was increased to 13% when a quartz reaction tube instead of a Pyrex one was used.

The introduction of a larger amount of oxygen into a Pyrex reaction zone, namely, 1 mole equivalent of oxygen per 100 moles of methylcyclopentane and 4 moles of aluminum bromide, caused the isomerization of 15% of methylcyclopentane; when a quartz reaction tube was used and irradiated, 42% of cyclohexane was formed.

In line with previous observations[1,4,5] it was noticed that the presence of about 0.04 mole per cent. of benzene in methylcyclopentane greatly reduces the degree of isomerization. The experimental results are summarized in Table I.

During the course of this study it was observed that aluminum bromide *per se* placed in a quartz tube and irradiated did not change coloration. It was noticed however that when aluminum bromide in the presence of oxygen was irradiated for 0.5-1 hour the tube was filled with brown vapors, which became more deeply colored as the time of irradiation increased. The mechanism by which the oxidation of aluminum bromide proceeds was not studied. It is very likely that the promoting effect of the oxygen is due to the oxidation of aluminum bromide with formation of bromine. The latter then reacts with methylcyclopentane to form bromomethylcyclopentane, which is a chain initiator for the isomerization.[6] The oxidation of aluminum bromide in solution in hydrocarbons seems to proceed even in diffused light.

The inhibiting effect of benzene upon the isomerization of methylcyclopentane is not entirely unexpected; it is most likely due to the removal of the chain initiator through the reaction with benzene, as has been shown previously.[1,5]

TABLE I

ISOMERIZATION OF METHYLCYCLOPENTANE

Expt.	Irradiation, hours	Reaction tube[b]	Methylcyclopentane used, moles × 10^2	Reactant charged moles per 100 moles of methylcyclopentane			Cyclohexane produced, %
				$AlBr_3$	O_2	C_6H_6	
1	18[a]	P	2.22	2.01	0.18	0	0
2	18[a]	P	3.10	4.00	1.05	0	15
3	18	P	2.11	2.02	0.18	0	6
4	18	Q	1.37	1.99	.17	0	13
5	18	Q	1.04	4.02	.96	0	42
6	18	Q	2.60	2.04	.20	0.037	0
7	18	Q	1.00	3.98	.96	0.039	6

[a] In experiments 1 and 2 the reaction tubes were not irradiated. [b] P, Pyrex reaction tube; Q, quartz reaction tube.

Experimental

The high vacuum apparatus and procedure have been described previously.[1,6] Linde oxygen was introduced into the apparatus through a phosphorus pentoxide drying tube. After being measured in the calibrated portion of the Töpler pump, the oxygen was transferred to an ampoule having a thin walled break-off. The sealed ampoule was carefully placed in the reaction tube, then the latter evacuated. After the other reactants had been added, the reaction tube was sealed off then shaken, in order to break the thin bulb of the ampoule containing oxygen. The composition of the hydrocarbons obtained from the reaction was determined by means of infrared absorption spectra.

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(1) For paper VII of this series see H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **72**, 4055 (1950).

(2) Universal Oil Products Company Predoctoral Research Fellow 1947-1949.

(3) H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 599 (1946).

(4) J. M. Mavity, H. Pines, R. C. Wackher and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).

(5) H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **71**, 749 (1949).

(6) H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

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The Structure of Methyl Acetylacrylate[1]

BY SAMUEL RAYMOND

Methyl acetylacrylate was first prepared in 1914 by Pauly, Gilmour and Will[1a] by the dehydro-

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(1) This work was supported by a grant from the National Institutes of Health and from the John and Mary R. Markle Foundation.

(1a) Pauly, Gilmour and Will, *Ann.*, **408**, 119 (1914).