retical potassium hydroxide dissolved in the least possible amount of water. The water was distilled out of the solution in an insulated boiling flask. The flame was then turned off and 80% of the theoretical amount of monochloro-2,7-dimethyloctane (based on the potassium hydroxide used) was dropped into the potassium cresolate at such a rate that the temperature (thermometer well in liquid) did not rise above 180°. The decylene distilled off as formed. The product was washed, dried and fractionated. Approximately six kilograms of decylene, boiling from 155–166° and representing a yield of 91.6% of the theoretical were thus obtained.

After a second fractionation, 90% of the principal fraction boiled between 159.6 and 162.8° (A. S. T. M. D 216); f. p. −79.5°; d_4^{20} 0.7418; n_D^{20} 1.4250.

A number of modifications of the described technique were tried. Each of these variations materially reduced the yield of the olefin.

Preparation of Decadiene

Direct treatment with potassium cresolate gave a poor yield in the case of dichloro-2,7-dimethyloctane (b. range 121–125° at 12 mm.; density at 20°, 1.0091; chlorine, by analysis 34.09%, theoretical 33.60%). On the other hand, long-continued boiling with a very large excess of alcoholic potash removed only one molecule of hydrochloric acid but gave a satisfactory yield of the chloro olefin. If the two methods were combined, a good yield of the diolefin was obtained. A chloro-2,7-dimethyloctene was obtained by refluxing the dichlorodimethyloctene with one and one-half moles of alcoholic potash (25% solution) for three hours. The chloro olefin was then treated with potassium cresylate by the method described above. It had a tendency to distil over unchanged and repeated treatment was necessary. The middle 90% of the carefully purified and fractionated product boiled over the range 161.0–166.0° at 764.4 mm.; f. p. −92.6°; d_4^{20} 0.7627; n_D^{20} 1.4410.

Both hydrocarbons were free from chlorine. The number of isomers present or the position of the double bonds was not established for either hydrocarbon. The decylene is apparently largely the 2,7-dimethyloctene (2), b. p. 159–162°, of Kishner.[3]

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(3) Kishner, *Chem. Zentr.*, II, 725 (1900).

UNITED GAS IMPROVEMENT CO.
PHILADELPHIA, PENNA.
RECEIVED APRIL 10, 1934

COMMUNICATIONS TO THE EDITOR

ISOBARIC ISOTOPES

Sir:

The recent publications of most scientists on the subject of isotopes imply that a given atom does not have an isobaric isotope.[1] However, it has been known for more than a decade that Uranium X_2 and Uranium Z[2] are not only isotopes but also isobars.

This example seems to indicate that, within the nucleus, the protons and negatrons or other units not only do not lose their identity completely but actually give rise to nuclear isomerism. If this hypothesis is correct, we should expect that isobaric isotopes should be as numerous as isomerism in the case of compounds. As yet, we have no means of showing the existence of such isotopes in the case of the non-radioactive elements but it is conceivable that the different isobaric isotopes may show differences in artificial disintegration or in artificial radioactivity recently discovered by the Joliots and confirmed by Lord Rutherford.

In all probability, these isomeric nuclei may have different energies of formation from protons and negatrons or other units and, if we accept the current hypothesis of the interconvertibility of mass and energy, may have slightly different atomic weights.

The symbols recently suggested by Harkins [*Science*, **79**, 138 (1934)] for distinguishing isotopes would be identical, and hence useless, for isobaric isotopes. A perfect system of symbols for distinguishing isotopes has, therefore, not yet been devised.

CHICAGO, ILLINOIS HERBERT J. BRENNEN
RECEIVED MAY 31, 1934

(1) The word "isobar" is used in the generalized sense, namely, for "atoms, the atomic weights of which may differ by small fractions of a unit."

(2) See, for example, Rutherford, Chadwick and Ellis, "Radiations from Radioactive Substances," New York, 1930, p. 24.

THE PEROXIDE EFFECT IN THE ADDITION OF REAGENTS TO UNSATURATED COMPOUNDS

Sir:

In a recent issue of THIS JOURNAL, Sherrill, Mayer and Walter [THIS JOURNAL, **56**, 926 (1934)] claim that the important factor governing addition of hydrogen bromide to pentene-1 is the solvent and not the peroxide content of the reaction mixture. In view of their report we have repeated the work on pentene-1, which was done in this Laboratory about a year ago (and as yet unpublished), and the tables below prove most conclusively that the 2-bromopentane is the "normal" product of the reaction while the 1-bromopentane is the peroxide-catalyzed, "abnormal" product of the reaction.

Table I is a summary of many experiments, and it is most significant that as long as added peroxides are absent, the 2-bromopentane is the only product of the reaction. Table II needs little interpretation. The striking fact about the addition recorded in that table is the completeness of the reversal of the addition in the presence of peroxides (as indicated by the sharpness of the boiling point of the addition product). Solvents, as may be noted, play very little part in governing the direction of addition.

TABLE I

ADDITION OF HYDROGEN BROMIDE TO PENTENE-1[a]

Conditions	B. p., °C.	n_D^{20}	Remarks
Simple addition	118–119	1.4414	The yields in all cases were 84% or better.
Thiocresol	118–119	1.4416	
Acetic acid	118–119	1.4415	
Thiocresol and light	117–119	1.4415	
Thiocresol and acetic acid	118–119	1.4414	
Acetic acid and light	117–118	1.4412	
Thiocresol, acetic acid and light	117–119	1.4416	
Thiocresol, light at 5 – 10°	117–119	1.4415	
Thiocresol, long evacuation	118–119	1.4413	
Thiocresol, separate drying	117–118	1.4418	
Thiocresol	118–119	1.4413	Pentene washed in the vapor phase to remove all possible traces of peroxides.
Diphenylamine	118–119	1.4412	
Hydroquinone	118–119	1.4418	
Thiocresol	118–119	1.4412	
Thiocresol at –80°	118–119	1.4413	

[a] The authors are indebted to Dr. Thomas M. Beck for most of the determinations recorded in this Table.

TABLE II

ADDITION OF HYDROGEN BROMIDE TO PENTENE-1

No.	Pentene, mole	HBr, mole	Agent added		Solvent and conditions	Time, hrs.	Yield, %	B. p., °C.	n_D^{20}	1-Bromopentane, %
1	0.15	0.21	Ascaridole	0.006	None, air	15.75	96	127.8–129.1	1.4442	97–100
2	.17	.19	Ascaridole	.008	Pentane, air	15	81	128.2–129.0	1.4443	100
3	.16	.20	Ascaridole	.011	HAc, air	12	51	118.2–119.5	1.4410	0
4	.17	.22	Ascaridole	.009	Propionic acid, vacuo	20	89	118.0–129.0	1.4423	40
5	.17	.24	Diphenylamine	.002	Pentane, vacuo	16.5	79	118.0–118.2	1.4410	0
6	.14	.21	Diphenylamine	.003	Propionic acid, vacuo	14	80	118.0–118.2	1.4410	0

It is noteworthy, and in agreement with our previous work, that in the presence of organic acids such as acetic and propionic acids, the peroxide effect should be less pronounced, and in conformity with that we find that acetic acid, even in the presence of peroxides, gives quantitative yields of the 2-bromopentane. The observation that, in passing hydrogen bromide into the cooled mixture of acetic acid and pentene, there is a separation of layers probably accounts for this product.

To overcome this difficulty we have modified in Run 4 our vacuum technique addition so as to bubble the hydrogen bromide slowly through a mixture of propionic acid, pentene and ascaridole. A yield of 40% of the 1-bromopentane was then obtained. We feel quite confident that the procedure can be further improved to yield quantitative yields of the 1-bromopentane even in the presence of glacial acetic acid as long as peroxides are added to the reaction mixture.

The technique of addition in all cases was the same as described in our previous papers [Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933)]. The bromopentanes obtained were identified, not only by their boiling points and indices of refractions, but by the preparation of the mercury compounds. The mercury compound of the 1-bromopentane melted sharply, without crystallization, at 121°, while the mercury compound from the 2-bromopentane was obtained as a low melting solid. It was therefore identified as the 3,5-dinitrobenzoate. Absolutely consistent determinations of the composition of the mixture were obtained by the use of all of these methods.

JONES CHEMICAL LABORATORY
UNIVERSITY OF CHICAGO
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M. S. KHARASCH
J. A. HINCKLEY, JR.
M. M. GLADSTONE

RECEIVED MAY 31, 1934

PREPARATION OF CRYSTALLINE β-*d*-[α-GALAHEPTOSE][1]

Sir:

Fischer [*Ann.*, **288,** 139 (1895)] prepared the two galaheptoses from galactose and crystallized β-galaheptose, but was unable to obtain α-galaheptose in crystalline condition. We have now succeeded in crystallizing this sugar.

The first crystalline material was obtained from an aqueous sirup resulting from the reduction of crystalline α-galaheptonic lactone in acid solution by sodium amalgam. Following removal of the sodium salt of α-galaheptonic acid by repeated treatments with methyl alcohol, the sirup crystallized after standing in a loosely covered beaker at laboratory temperature for several weeks. With these crystals it was possible to nucleate other sirups and obtain crystallization readily.

β-*d*-(α-Galaheptose) monohydrate crystallizes in clusters of colorless glistening prisms, stable at room temperature upon drying *in vacuo* over calcium chloride or sulfuric acid. When slowly heated in a capillary tube it melts at 77–78° (corr.) to a colorless sirup. Its solution in water shows $(\alpha)^{20}_{\mathrm{D}}$ $-22.5°$ for the monohydrate after three minutes and an equilibrium value of $-14.1°$ in 180 minutes, at 20°. These data establish the fact that the sugar is the less dextrorotatory form of a sugar in the *d*-series, and according to the usual nomenclature [Hudson, THIS JOURNAL, **31,** 66 (1909)] it is to be designated as the β-form. Studies of the *d*-galaheptoses, which closely resemble *l*-mannose and *l*-glucose in configuration, are in progress.

[1] Publication authorized by the Surgeon General, U. S. Public Health Service.

NATIONAL INSTITUTE OF HEALTH
WASHINGTON, D. C.
RAYMOND M. HANN
ALICE T. MERRILL
C. S. HUDSON

RECEIVED JUNE 4, 1934

PHOTOCHEMICAL DECOMPOSITION OF KETENE

Sir:

In a recent paper Ross and Kistiakowsky [THIS JOURNAL, **56,** 1112 (1934)] have confirmed our experimental results on the photochemical decomposition of ketene [*J. Chem. Soc.*, 1533 (1933)]. They have in addition measured the quantum efficiency and find average values of about 1.0 at 3130 Å. and 0.3 at 3650 Å. While agreeing with our primary change

$$CH_2{=}CO \longrightarrow CH_2 + CO$$

they suggest that the secondary change

$$CH_2 + CH_2 \longrightarrow C_2H_4$$

is in better agreement with the unit quantum yield at 3130 Å. than is that postulated by us

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO + 9 \text{ k. cal.}$$

This reaction cannot, however, be eliminated on such evidence alone. It is not necessarily true that the higher of the two values of the quantum efficiency is its maximum value. Further, it is now apparent that for polyatomic molecules the quantum yield of the primary reaction may be less than unity throughout a considerable portion of a region of continuous absorption. This is true of acetone (γ = 0.2 for λ 3130 and 0.4 for λ 2650) as has been shown by Damon and Daniels [THIS JOURNAL, **55,** 2363 (1933)] and recently confirmed by us. If the radiationless transition which follows absorption of light be viewed as an Auger effect confined to the carbon atom of the chromophoric (carbonyl) group, we may suppose that it does not in all cases lead to dissolution of the C=C link but that instead it may lead to the degradation of the electronic energy of excitation to molecular vibration, and its dissipation as heat. The relative probabilities of these alternatives would not be expected to remain constant throughout the absorption band but as the wave length of the absorbed radiation decreased the fraction of molecules decomposing would increase.

The spectroscopic observations of ketene made by Lardy [*J. chim. phys.*, **21,** 353 (1924)] and ourselves (Ref. 2) are completely in agreement with these ideas. The absorption spectrum consists of completely diffuse bands throughout its *entire* range. The substance shows no fluorescence. The low quantum yield of 0.3 at λ 3650 increases to 1.1 at λ 3130 (Ref. 1) in full agreement with this theory. As with acetone the value of the quantum yield may be expected to increase toward the theoretical maximum value as the magnitude of the absorbed quantum exceeds by greater amounts the energy necessary to decompose the molecule. This would lead to