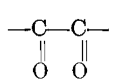
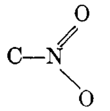
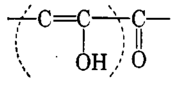
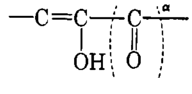
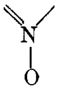
TABLE VIII

GROUP FREQUENCY RANGE, cm.$^{-1}$

Compound	 1730 and 1710	 1570–1500 and 1370–1300		[a]	 1300–1225	Bands present in quinoxalines but absent in glyoxals
I[b]	1730 and 1709	1534 and 1352	. .	. . .	. . .	
II	?	1535 and 1334	3400	1674 and 1632	. . .	
IV	?	1530 and 1355	3400	1665 and 1630	. . .	
V	?	1535 and 1352	3433	1689 and 1667	. . .	
VI	. . .	1525 and 1334	. .	. . .	. . .	1108 and 1006
VII	. . .	1529 and 1349	. .	. . .	. . .	1113 and 1007
VIII	. . .	1533 and 1349	. .	. . .	. . .	1113 and 1007
IX	. . .	1523 and 1348	. .	. . .	. . .	1114 and 1006
X	. . .	1540 and 1352	. .	. . .	. . .	1113 and 1007
XII	. . .	. . .	. .	. . .	1252 and 1208	
XIII	. . .	. . .	. .	. . .	1253 and 1214	
XIV	. . .	. . .	. .	. . .	1263 and 1219	
XV	. . .	. . .	. .	. . .	1250 and 1212	

[a] R. P. Barnes and G. E. Pinkney, *J. Am. Chem. Soc.*, **75**, 479 (1953). [b] M.p. 152°.

a result of quinoxaline formation. However, there are features in the spectra of some of the quinoxalines that suggest increased conjugation.

The spectra of the ring closure products clearly indicate (1) the absence of the nitro group; and (2) absorption in the 1300–1200-cm.$^{-1}$ region which is reported to be characteristic of pyridine N-oxides.

A Convenient Method for the Preparation of 1-Methylcyclobutene

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1-Methylcyclobutene (II) can serve as a convenient starting material for the preparation of various cyclobutane and cyclobutene derivatives in a way comparable to the synthetic use of larger ring homologues. For instance, by applying the hydroboration procedure of Brown and Zweifel[1] II can readily be converted into *trans*-2-methylcyclobutanol (III), and further, the tosylate of III can be decomposed at 130–135° to yield 3-methylcyclobutene by *trans* elimination.[2]

Compound II is usually prepared[3,4] by hydroiodination of methylenecyclobutane (I), followed by dehydrohalogenation of the resulting 1-iodo-1-methylcyclobutane, which gives a nearly equimolar mixture of I and II. The over-all yield of II by this method is only 20–25%. Recently, it has been reported[5] that II is obtained as the main product in the sodium methoxide-catalyzed decomposition of cyclopropyl methyl ketone tosylhydrazone in Diethyl Carbitol. Although this ring-expansion reaction is of potential interest, it does not seem to have been examined as a preparative method.

It should be recalled that most of the ordinary olefin-forming reactions cannot be applied in the present case. For example, dehydration of 1-methylcyclobutanol (IV) in the presence of acid catalysts or refluxing of IV with iodine fail to produce II.[3] Further, procedures involving high temperature treatment (above 200°) are unfavorable for the synthesis because of the low thermal stability[6] of II. Thus, attempted isomerization of I over alumina at 300° gives isoprene instead of II,[3,7] while the decomposition at 255° of O-1-methylcyclobutyl-S-methyl xanthate[8] yields mainly isoprene (57%) and only 25% of II.

Recent work[9] in this laboratory has led to a revision of the previously expressed view[10] that "methylenecyclobutane shows no tendency to rearrange into methylcyclobutene." In the presence of a sodium-alumina catalyst[11] compound I isomerizes into II and equilibrium is rapidly attained at room temperature.

I II

$(K_{\text{II/I}} = 5.7 \text{ at } 25°)_{\mu}$

By applying the following conditions a procedure has now been developed (see Experimental) which allows the use of the above reaction as a convenient preparative method: (a) the isomerization temperature is lowered to 0–3° to avoid losses due to volatility and possible side reactions, *e.g.*, polymerization; (b) the catalyst–olefin weight ratio is reduced to 1:6; and (c) a suitable desorption technique is applied at the end of the reaction.

The product at 2° (recovery, 95%) contains 86% of II and 14% of I; *i.e.*, the yield of II based on converted I is practically quantitative. II is separated from the higher boiling I by fractional distillation.

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(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(2) E. Gil-Av and J. Shabtai, unpublished data.

(3) W. Shand, Jr., V. Schomaker, and J. R. Fischer, *J. Am. Chem. Soc.*, **66**, 636 (1944).

(4) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957).

(5) L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960).

(6) J. Herling, J. Shabtai, and E. Gil-Av, *Bull. Res. Council Israel*, **11A**, 20 (1962).

(7) M. Dojarenko, *Ber.*, **59**, 2933 (1926).

(8) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

(9) E. Gil-Av and J. Herling, *Tetrahedron Letters*, **1**, 27 (1961).

(10) R. A. Raphael, "Chemistry of Carbon Compounds," Vol. II^a, E. H. Rodd, Ed., Elsevier Publishing Co., Amsterdam, 1953, p. 52.

(11) H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958); W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960).

Highly purified samples of I (>99.8 mole %) and of II (>99.3 mole %) were prepared in the present work and their infrared spectra measured in the liquid state (see Table I).

TABLE I

FREQUENCIES OF SIGNIFICANT INFRARED ABSORPTION MAXIMA[a] OF METHYLENECYCLOBUTANE (I) AND 1-METHYLCYCLOBUTENE (II), IN cm.$^{-1}$

I—3083 (w,) 2990 (s), 1760 (m), 1680 (s) ,1423 (s), 1393 (w), 1251 (w), 1222 (w), 1199 (w), 1170 (m), 1075 (m), 1026 (w), 956 (w), 887 (s), 792 (w), 767 (w), 736 (w)

II—3325 (w), 3170 (w), 3050 (m), 2910 (s), 2721 (m), 2295 (w), 2165 (w), 2105 (w), 2025 (w), 1820 (w), 1761 (w), 1724 (m), 1640 (s), 1584 (m), 1437 (s), 1374 (m), 1276 (s), 1212 (w), 1188 (s), 1172 (s), 1088 (m), 1033 (m), 984 (s), 952 (s), 895 (m), 857 (s), 732 (s)

[a] Intensity: s, strong; m, medium; w, weak.

A previously published[12] spectrum of I in the liquid state contains not only the most prominent bands[13] of contaminating spiropentane (at 782, 990, 1051 and 1155 cm.$^{-1}$), but, as shown by comparison with the present data, even the medium intensity absorptions of the same impurity in the vicinity of 2015, 2310 and 2420 cm.$^{-1}$. A more recent spectrum,[14] measured on a purer specimen of I (but still containing some spiropentane, as indicated by a band of medium intensity in the vicinity of 990 cm.$^{-1}$), does not provide sufficient detail on the position of the absorption maxima.

Previously published data[12] on II include several bands, *e.g.*, at 804, 1110, 1130, 1345 and 1670 cm.$^{-1}$, which are absent in the present spectrum. The rather strong foreign band at 1670 cm.$^{-1}$ is obviously due to contaminating I.

The n.m.r. spectrum of II was also measured. It showed: (1) a doublet at 1.66 p.p.m. ($J = 2$ c.p.s.), due to the methyl group situated at the double bond; (2) a rather sharp line at 2.38 p.p.m., arising from the allylic hydrogens; and (3) a closely split signal centered at 5.60 p.p.m., due to the vinylic hydrogen. The relative intensities of the three signals were in the ratio 3:4:1, respectively.

Experimental

Methylenecyclobutane (I).—The commercially available I contained 16% of 2-methyl-1-butene and 4% of spiropentane as side products. I of about 99% purity was obtained by fractional distillation on a 70-plate spinning band column. The best portion of the distillate (>99.8 mole %) had b.p. 41.3° at 760 mm., n^{20}_{D} 1.4212.

Preparation of 1-Methylcyclobutene (II). Isomerization Procedure.—The alumina (Alcoa, grade F-1, 100 mesh) was pretreated at 300–320° under nitrogen for 24 hr., and employed immediately afterwards. In a typical catalyst preparation 12 g. of alumina was introduced into a three-necked flask equipped with a condenser, a dropping funnel, and a mechanical stirrer provided at its end with a semicircular impeller. The system, was purged with nitrogen, and the alumina was heated to 140°, at which point 2 g. of sodium was added. Mixing at 140° was continued for 20 min. and the black-colored catalyst obtained was cooled to 2–3° in an ice–water bath. A 50-g. sample of I was added in one portion to the flask; it is essential to use material freshly distilled over sodium, since samples not so treated deactivate the catalyst. The flow of nitrogen was reduced to a minimum and iced water circulated through the condenser. Stirring was continued for 2 hr., keeping the temperature below 5°. At the end of this period the supernatant liquid was quickly decanted into a precooled flask. The rest of the product, partly adsorbed on the catalyst, was recovered by distillation at 100 mm. into a Dry Ice–acetone trap. The total liquid weighed 47 g. (recovery, 94%) and contained 86% of II. Fractional distillation on the above column gave II, about 99% pure. The best portion of the distillate (>99.3%) had b.p. 37.3° at 760 mm., n^{20}_{D} 1.4081.

Analysis.—The purity of the olefin samples was determined by gas chromatography using silver nitrate–glycol[15] as the stationary phase. The infrared spectra were measured with a Model IR 7 Beckman spectrophotometer. A Varian A-60 spectrometer was employed for the measurement of the n.m.r. spectrum of II, using carbon tetrachloride as solvent and tetramethylsilane as the reference compound.

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[13] F. F. Cleveland, M. J. Murray, and W. S. Gallaway, *ibid.*, **16**, 158 (1948).

[14] D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).

[15] J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatog.*, **11**, 32 (1963); **8**, 349 (1962).

Preparation of 2-Bromo-3-methylbutane by the Radical Addition of Hydrogen Bromide to 2-Methyl-2-butene

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During the course of an investigation of the pyrolysis of olefins, a quantity of 2-bromo-3-methylbutane was desired. A search of the literature revealed that details concerning the synthesis and isolation of this structurally simple bromide were lacking.[2] Needless to say, this bromide has not been obtained in satisfactory yields from 3-methyl-2-butanol.[2] Although the peroxide-catalyzed addition of hydrogen bromide to 2-methyl-2-butene appeared to be the most suitable approach, the literature is filled with inconsistencies concerning the best conditions for, and the products obtained from, such an addition. In many instances products were merely detected but not isolated, the reactions were run on very small quantities of material, and no yields were reported. Low temperature,[3] no sol-

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[1] American Chemical Society Petroleum Research Fund Fellow, 1959–1961; Celanese Fellow, 1961–1962; Goodyear Tire and Rubber Co. Fellow, 1962.

[2] For some of the problems involved in the preparation of 2-bromo-3-methylbutane from 2-methyl-2-butene, 3-methyl-2-butanol, or 3-methyl-1-butene see E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc. New York, N. Y., 1954 pp. 271–247 and pp. 367–411; A. Michael and N. Weiner, *J. Org. Chem.*, **5**, 395 (1940).

[3] A. Michael and N. Weiner, *ibid.*, **4**, 531 (1939).

[4] F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).

[5] F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, **7**, 491 (1942).

[6] W. E. Vaughan, F. F. Rust, and T. W. Evans, *ibid.*, **7**, 477 (1942).