the groups of isomers involved in the reactions chosen for this work.

When triisopropylborane (I) was heated in the 135–146° range under dry nitrogen, these isomerizations

$$\underset{\text{I}}{(i\text{-Pr})_3\text{B}} \rightleftharpoons \underset{\text{II}}{(i\text{-Pr})_2\text{B}(n\text{-Pr})} \rightleftharpoons (i\text{-Pr})\text{B}(n\text{-Pr})_2 \rightleftharpoons \underset{\text{IV}}{(n\text{-Pr})_3\text{B}}$$
$$\text{III}$$

proceeded slowly to equilibrium mixtures. These mixtures were distillable *in vacuo* below 100° without disproportionation or isomerization, and were analyzed readily by gas–liquid chromatography (g.l.c.) over "Silicone 550" at 97°. Fortunately, this analytical procedure revealed the exact distribution of isopropyl and *n*-propyl groups among the four isomers. The equilibrium mixtures contained chiefly, IV, some III, very little II, and no I. The equilibrium composition at 146° was determined in two ways: (a) heating of IV for 47 hr. gave a mixture containing 0.5% II, 14% III, and 85.5% IV; (b) a mixture originally containing 1% II, 23% III, and 76% IV heated for 37 hr. gave a product containing 0.5% II, 16% III, and 83.5% IV. The equilibrium composition at 135° was similarly determined: (a) IV heated for 72 hr. gave a product having no I, <0.1% II, 10% III, and 90% IV; (b) heating a mixture originally containing 15.8% III and 84.2% IV for 147 hr. gave a product containing no I, < 0.3% II, 14.4% III, and 85.6% IV.

Similar results were obtained by heating tri-*sec*-butylborane (V) and tri-*n*-butylborane (VIII). In these instances, however, direct analysis by g.l.c. failed and the equilibrium mixtures could be analyzed only by determination of the relative amounts of *sec*-butyl and *n*-butyl alcohols produced by hydrogen peroxide oxidation. Analysis of ethereal solutions of these alcohols was accomplished very well by g.l.c. over "Ucon Polar" at 115°. Heating of either V at 191° for 26 hr. or VIII at 190° for 7 hr. or 14 hr. gave, after oxidation, 6% *sec*-butyl alcohol and 94% *n*-butyl alcohol. These data indicate, by analogy with the *n*-propyl *vs.* isopropyl case, the equilibrium composition of butylboranes to be as follows: no V, trace of di-*sec*-butyl-*n*-butylborane (VI), 18% di-*n*-butyl-*sec*-butylborane (VII), and 82% VIII at 190–191°.

Thermal isomerization of diisobutyl-*t*-butylborane[4] (IX) gave a significantly different result in that the formation of triisobutylborane (X) was essentially irreversible. Thus, heating of X for 20 hr. in one experiment and for 35 hr. in another, both at 135°, followed by peroxide oxidation and g.l.c. gave isobutyl and *t*-butyl alcohols in a ratio greater than 99.7:0.3. When X was heated for 7 hr. at 186° similar analysis gave the alcohols in the ratio 99.3:0.7. A mixture originally containing 7.2% IX and 92.8% X, heated for 23 hr. at 188° gave, after oxidation, isobutyl and *t*-butyl alcohols in a 99.5:0.5 ratio. Furthermore, the kinetics of the isomerization of IX to X at five temperatures between 125 and 150° indicate a clean, irreversible unimolecular process.

The data presented above permit the following conclusions: (a) for the equilibrium III $\rightleftharpoons$ IV at 146°, $K \simeq 5.7$ and $\Delta F = -1.4 \pm 0.06$ kcal./mole; at 135°, $K \simeq 7.5$ and $\Delta F = -1.6 \pm 0.1$ kcal./mole; (b) for VII $\rightleftharpoons$ VIII at 190°, $K \simeq 4.5$ and $\Delta F \simeq -1.4$ kcal./mole; (c) for IX $\rightleftharpoons$ X at 135°, $K > 99$ and $\Delta F > -3.7$ kcal./mole; at 186°, $K \simeq 54$ with $\Delta F \simeq -3.5$ kcal./mole. These findings supplement those of Brown[3] and establish that the stability of alkyl groups attached to boron is primary > secondary ≫ tertiary. It should be noted also that the equilibrium mixtures of trialkylboranes contain the unsymmetrical isomers (*e.g.*, II and III) which survive without disproportionation.

The kinetics and the mechanisms of these isomerizations will be discussed in a later communication.

(4) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958).

Experimental

Trialkylboranes.—Triisopropyl- (I), tri-*n*-propyl- (IV), tri-*sec*-butyl- (V), tri-*n*-butyl- (VIII), and triisobutylborane (X) were prepared by the alkylation of boron trifluoride (as the etherate) with the appropriate Grignard reagent in anhydrous ether.[5] Products were fractionally distilled *in vacuo;* a high degree of isomer purity was established in each case by oxidation to the corresponding alcohol,[6] easily recognized by g.l.c. Compounds I and IV were also checked directly by g.l.c. and were observed to give single, distinct, and reproducible peaks. Diisobutyl-*t*-butylborane (IX) was prepared from *t*-butyl chloride, boron trifluoride, and magnesium in anhydrous ether as previously described.[4]

Product Analysis.—Gas–liquid chromatography was accomplished with the "Kromo-Tog I" and 2-m. columns supplied by Hypren Co., Pittsburgh, Pa. Alcohols, singly or in mixtures, were recognized by comparison with authentic samples using "Ucon Polar" columns at *ca.* 115°. The propylboranes were resolvable with "Silicone 550" columns at 97°. Higher trialkylboranes were decomposed during g.l.c. over all columns used; in these cases analysis could be made only *via* the alcohols produced by oxidation.

(5) E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

(6) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

The Preparation of Some Benzyl-*o*-nitrophenylglyoxals and Cyclization of Their Quinoxalines

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Received December 12, 1962

C. W. Muth, *et al.*,[3,4] have reported examples in the biphenyl series of the condensation of a nitro group in the 2-position with an activated methylene group in the 2′-position with the production of cyclic amine oxides.

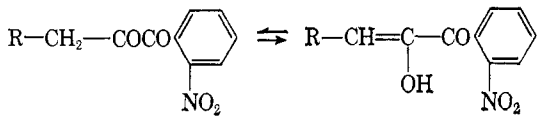
With the idea that benzyl-*o*-nitrophenylglyoxals might similarly lead to substituted quinoline N-oxides, we prepared the following glyoxals.

(1) Taken from Ph.D. thesis, Howard University, 1959.

(2) In partial fulfillment of the requirements for the M. S. degree.

(3) C. W. Muth, J. C. Ellers, and O. F. Folmer, *J. Am. Chem. Soc.*, **79**, 6500 (1957).

(4) C. W. Muth, N. Abraham, L. Linfield, R. B. Wotring, and E. A. Pacofsky, *J. Org. Chem.*, **25**, 736 (1960).



I-V

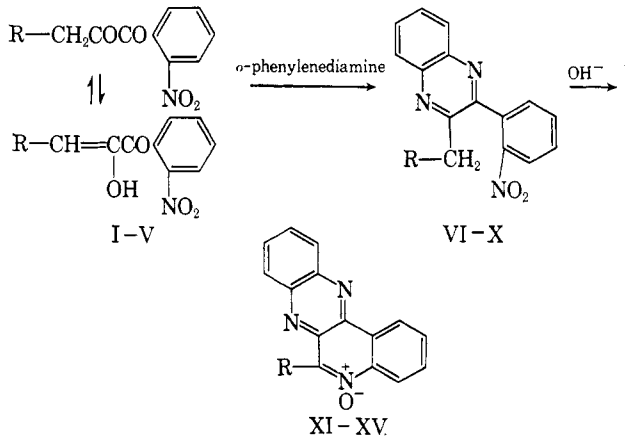
I, R = mesityl
II, R = *p*-tolyl
III, R = *o*-chlorophenyl
IV, R = *p*-chlorophenyl
V, R = phenyl

Preparation of the glyoxals involved the use of chalcones which were obtained from *o*-nitroacetophenone[5] and the appropriate aldehyde. The chalcones were converted to the ethylene oxides[6] and the α-N-diethylaminochalcones[7] as parent substances of the glyoxals.

Isomerization of 1-mesityl-2-*o*-nitrobenzoylethylene oxide in boiling methanolic potassium hydroxide with subsequent acidification led to a good yield of both the ketonic and enolic modifications of glyoxal I. Under the same conditions the other ethylene oxides reacted vigorously with the production of products other than the glyoxals. Other methods of preparation of glyoxals[8-10] failed to give significant yields of glyoxals II, III, IV, and V. However, these glyoxals were obtained in good yield by way of the α-N-diethylamino chalcones according to Cromwell.[7] The method of Kohler and Weiner[11] likewise produced the glyoxals in good yield (see Table V).

Attempts to effect ring closure to the quinoline N-oxides by refluxing the glyoxals with methanolic potassium hydroxide failed, and the glyoxals could not be recovered except in the case of I, upon acidification of the medium.

All of the glyoxals yielded quinoxalines (VI–X) (see Table VI), which upon treatment with boiling methanolic potassium hydroxide underwent cyclization to the quinoxaline of 2-aryl-3,4-diketoquinoline N-oxides (XI–XV) (see Table VII).

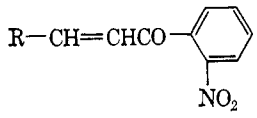


I-V VI-X XI-XV

Experimental[12]

Preparation of the Chalcones.—To a stirred solution of equivalent amounts of *o*-nitroacetophenone[5] and the appropriate aldehyde in methanol, was added in one portion, the equivalent amount of potassium hydroxide dissolved in a small volume of water. The temperature of the resulting solution was kept below 25°. Generally the condensation took place in a few minutes and the product separated as crystals or an oil which crystallized on standing. The product was then filtered, washed several times with water to remove the alkali, then with alcohol, and recrystallized from alcohol (see Table I).

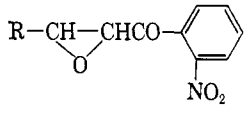
TABLE I



R	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Mesityl	80–81	$C_{18}H_{17}NO_3$	73.2	73.8	5.8	6.2
p-Tolyl	134–135	$C_{16}H_{13}NO_3$	71.9	72.4	4.9	4.3
p-Chlorophenyl	123–124	$C_{15}H_{10}NO_3Cl$	62.7	62.7	3.5	3.8
o-Chlorophenyl	88–89	$C_{15}H_{10}NO_3Cl$	62.7	62.7	3.5	3.9
Phenyl	128	$C_{15}H_{11}NO_3$	71.1	71.9	4.4	4.7

Preparation of the 1-Aryl-2-*o*-nitrobenzoylethylene Oxides.—The ethylene oxides were prepared according to the method of Weitz and Scheffer[6] with the single modification of the addition of a small amount of 1,4-dioxane to increase the solubility of the chalcones, and the addition of water after 30 min. of reaction time to precipitate the oxides (see Table II).

TABLE II



R	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Mesityl	148–149	$C_{18}H_{17}NO_4$	69.5	69.8	5.5	5.5
p-Tolyl	95–96	$C_{16}H_{13}NO_4$	67.8	67.9	4.6	4.6
p-Chlorophenyl	94–95	$C_{15}H_{10}NO_4Cl$	59.3	59.5	3.3	3.4
o-Chlorophenyl	107	$C_{15}H_{10}NO_4Cl$	59.3	59.6	3.3	3.4
Phenyl	79–80	$C_{15}H_{11}NO_4$	66.9	67.0	4.1	4.2

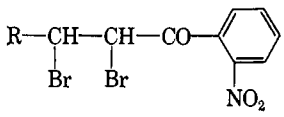
Preparation of the Chalcone Dibromides.—To a solution of the chalcone in either chloroform or methylene chloride was added dropwise, with stirring, an equivalent quantity of bromine in solution of the selected solvent. When the color of the bromine was discharged, the solvent was removed *in vacuo*. The resulting solid was washed with cold methanol until it was white. In the case of benzal-*o*-nitroacetophenone dibromide, an oil was obtained which crystallized upon chilling. This dibromide was purified by recrystallization from an ethyl acetate–petroleum ether mixture (see Table III).

Preparation of the α-N-Diethylaminochalcones.—These compounds were prepared according to Cromwell[7] (see Table IV).

Preparation of the Glyoxals. Method A. Glyoxal I.—To a solution of 9.0 g. of potassium hydroxide in 75 ml. of hot methanol was added slowly, with stirring, 15 g. of 1-mesityl-2-*o*-nitrobenzoylethylene oxide. The solution turned red and began to boil. The solution was kept boiling for 10 min., then cooled and neutralized with dilute hydrochloric acid. The resulting oil solidified as reddish brown crumbles. It was filtered, washed with water, dried, and recrystallized from methanol, yielding

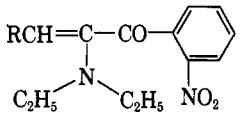
(5) G. A. Reynolds and C. R. Hauser, *Org. Syn.*, **30**, 70 (1950).
(6) E. Weitz and A. Scheffer, *Ber.*, **54**, 2344 (1921).
(7) N. H. Cromwell, *J. Am. Chem. Soc.*, **62**, 1673 (1940).
(8) E. P. Kohler and R. P. Barnes, *ibid.*, **56**, 211 (1934).
(9) H. O. House, *ibid.*, **76**, 1235 (1954).
(10) A. H. Blatt, *ibid.*, **61**, 3494 (1939).
(11) E. P. Kohler and N. Weiner, *ibid.*, **56**, 434 (1934).
(12) All analyses were performed by the junior author, Dr. Joseph H. Graham, of the Food and Drug Administration, the Division of Pharmaceutical Chemistry, Washington 25, D. C.

TABLE III



R	Solvent	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Tolyl	$CHCl_3$	164.5	$C_{16}H_{13}NO_3Br_2$	45.0		3.1	
					45.8		3.4
p-Chlorophenyl	$CHCl_3$	167–168	$C_{15}H_{10}NO_3ClBr_2$	40.2		2.3	
					40.4		2.8
o-Chlorophenyl	CH_2Cl_2	159–161	$C_{15}H_{10}NO_3ClBr_2$	40.2		2.3	
					40.6		2.1
Phenyl	CH_2Cl_2	109	$C_{15}H_{11}NO_3Br_2$	43.6		2.7	
					43.9		2.7

TABLE IV



R	M.p.,°C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Tolyl	66–67	$C_{20}H_{22}N_2O_3$	70.9		6.6	
				71.3		6.4
p-Chlorophenyl	95–96	$C_{19}H_{19}N_2O_3Cl$	63.6		5.4	
				63.0		5.8
o-Chlorophenyl	91–92	$C_{19}H_{19}N_2O_3Cl$	63.6		5.4	
				63.6		5.6
Phenyl	57–59	$C_{19}H_{20}N_2O_3$	70.4		6.2	
				70.1		6.5

7.0 g. of yellow solid, melting at 152°. This material did not produce color with alcoholic ferric chloride immediately, but upon long standing a deep reddish brown color developed.

The filtrate obtained from this recrystallization was made strongly acidic with hydrochloric acid and further diluted with water. A pale yellow solid separated which was filtered, washed, dried, and recrystallized from methanol, yielding 5.5 g. of pale yellow needles which melted at 133°. This material produced a red color instantaneously with alcoholic ferric chloride.

The parent isomeric ethylene oxides of glyoxals II, III, IV, and V underwent violent decomposition with hot methanolic potassium hydroxide. No glyoxals could be isolated.

Method B. Glyoxals II, III, IV, and V were obtained in good yield by the method of Kohler and Weiner.[11]

TABLE V

Glyoxal	Method of preparation	M.p., °C.	Formula	Carbon, % (Calcd.)	Carbon, % Found	Hydrogen, % (Calcd.)	Hydrogen, % Found
I	A	133					
		152	$C_{18}H_{17}O_4N$	(69.5)		(5.5)	
	B	133			69.4		5.4
		152			69.8		5.7
			$C_{16}H_{13}NO_4$	(67.8)		(4.6)	
II	B	130			67.7		4.7
	C	116-118			67.8		4.8
			$C_{15}H_{10}NO_4Cl$	(59.3)		(3.3)	
III	B	89			59.1		3.5
	C	88–89			59.0		3.5
			$C_{15}H_{10}NO_4Cl$	(59.3)		(3.3)	
IV	B	151			59.6		3.5
	C	139–141			59.8		3.6
			$C_{15}H_{11}NO_4$	(66.9)		(4.1)	
V	B	112			66.7		4.3
	C	94–95			66.5		4.2

Method C. Glyoxals II, III, IV, and V also were obtained in good yield by way of the α-N-diethylaminochalcones according to Cromwell.[7]

All of these glyoxals undergo alkaline hydrogen peroxide cleavage giving rise to *o*-nitrobenzoic acid and the corresponding substituted phenylacetic acid.

Glyoxal I, upon refluxing with methanolic potassium hydroxide with subsequent acidification, was recovered unchanged, whereas glyoxals II, III, IV, and V underwent violent decomposition.

The 2-Benzyl-3-*o*-nitrophenylquinoxalines (VI–X).—A solution of the diketone and an equivalent quantity of *o*-phenylenediamine in methanol was refluxed for about 1 hr. Upon chilling, the quinoxaline crystallized in light cream-colored needles which were purified by recrystallizetion from methanol.

These quinoxalines produced a red color with concentrated sulfuric acid.

TABLE VI

Compound	R	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
VI	Mesityl	165	$C_{24}H_{21}N_3O_2$	75.2		5.5	
					75.0		5.7
VII	*p*-tolyl	100	$C_{22}H_{17}N_3O_2$	74.3		4.8	
					74.2		5.1
VIII	*p*-Chlorophenyl	147–149	$C_{21}H_{14}N_3O_2Cl$	67.1		3.8	
					67.4		3.8
IX	*o*-Chlorophenyl	92	$C_{21}H_{14}N_3O_2Cl$	67.1		3.8	
					67.3		4.0
X	Phenyl	126–127	$C_{21}H_{15}N_3O_2$	74.0		4.4	
					74.3		4.9

The Quinoxalines of the 2-Aryl-3,4-diketoquinoline N-Oxides (XI–XV).—A solution of 0.5 g. of the quinoxaline (VI–X) in 15 ml. of methanol was mixed with a solution of 1.0 g. of potassium hydroxide in 15 ml. of methanol and boiled for about 15 min. Upon cooling, a deep yellow solid began to separate. The solid was filtered, washed, and dried.

TABLE VII

Compound	R	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
XI	Mesityl	250	$C_{24}H_{19}N_3O$	78.9		5.2	
					79.3		5.4
XII	*p*-Tolyl	240–241	$C_{22}H_{15}N_3O$	78.3		5.2	
					78.7		5.4
XIII	*p*-Chlorophenyl	254–255	$C_{21}H_{12}N_3OCl$	70.5		3.4	
					70.0		3.7
XIV	*o*-Chlorophenyl	256	$C_{21}H_{12}N_3OCl$	70.5		3.4	
					70.9		3.7
XV	Phenyl	239–240	$C_{21}H_{13}N_3O$	78.0		4.0	
					78.5		4.4

Spectroscopic Analysis.—The infrared spectra of the following compounds involved in this study have been recorded from potassium bromide disks using a Perkin-Elmer Model 21 infrared spectrophotometer: (1) the diketones (enols) I, II, IV, and V; (2) the quinoxalines VI–X); and (3) the ring closure products XII–XV (see Table VIII).

The analysis of the spectra, without benefit of similarly obtained spectra of less complex compounds having similar structural units, does not permit actual confirmation of the structures proposed—particularly in the case of the ring closure products.

The spectra of the diketones indicate that (1) they exist essentially in the enolic modification with the exception of I which is essentially ketonic; (2) differences in degree of association of the enol form exist within the series; and (3) they are aromatic and contain a conjugated nitro group.

The spectra of the corresponding quinoxalines show (1) none of the hydroxyl or carbonyl absorption seen in the diketones or enols; and (2) retention of the characteristic nitro group absorption. No absorption bands could be unequivocally assigned as

TABLE VIII

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

Compound	—C(=O)—C(=O)—	C(=O)—N(=O)—C	—C(OH)=C—C(=O)—	—C(OH)=C—C(=O)—	N(=O)	Bands present in quinoxalines but absent in glyoxals
	1730 and 1710	1570–1500 and 1370–1300			1300–1225	
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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The Weizmann Institute of Science, Rehovoth, Israel

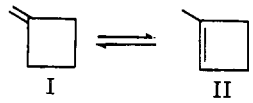
Received April 4, 1963

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

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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