COMMUNICATIONS

octene-1 (described in a previous communication). Both 1-tert-butylperoxyoctene-2 and 3-tert-butyl-peroxyoctene-1 are formed as by-products.

The formation of α-cumyl benzoate from cumene, equimolar amounts of tert-butyl hydroperoxide and benzoic acid in the presence of trace amounts of copper salts proceeds less readily and shows a remarkable solvent effect. The highest yield, 20%, is obtained in excess cumene, in the presence of less than 0.2 mol % catalyst. Increased amounts of catalyst decrease the yield in favor of the α-cumyl tert-butyl peroxide, which is always the major product. When benzene or tert-butyl alcohol is used as a solvent, in the presence of 1.5 mole of cumene and 0.002 moles copper chloride, α-cumyl benzoate is formed in yields of only 11% and 6%, respectively. With nitrobenzene pyridine, acetic acid, or heptane as the solvent, no benzoate could be detected.

When tert-butyl hydroperoxide (one mole) was added over a period of 3 hours at 80° to a suspension of phthalimide (one mole) in a benzene (10 moles) solution of cyclohexene (1.5 moles) containing 0.002 mole cuprous chloride, N-cyclohexenyl phthalimide (0.14 mole) was isolated. (M.p., 114.5°, from alcohol. Anal. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16; mol. wt., 227. Found: C, 73.96; H, 6.0; N, 6.16; mol. wt. 240. Unsaturation 100% by ozonolysis.) Its infrared spectrum is in agreement with the assigned structure. A solvent effect similar to the one observed with α-cumyl benzoate is found. Best solvents are benzene, xylene, acetonitrile, and ethyl acetate. Work in progress indicates that with tert-butyl peroxide as oxidizing agent this reaction is almost quantitative. It also indicates that saccharin and pyrimidine are also able to give N-substituted products.

Substitution is observed also in radical reactions of the conventional type. Decomposition of di-tert-butyl peroxide in cumene, in the presence of benzoic acid yields about equal amounts of dicumene and α-cumyl benzoate. However, addition of one mole per cent cuprous chloride inhibits completely the formation of dicumene but increases the yield of α-cumyl benzoate.

The solvent effect observed in these reactions indicates that the radicals form a loose complex with the solvent. The most suitable solvents are those which are known to give stable complexes with triphenyl methyl radicals.[1]

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(1) M. Gomberg and L. H. Cone, Ber., 38, 1333 (1905).
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Disproportionation Reaction of Diphenylsilane in the Absence of Any Added Catalyst

Sir:

Disproportionation reactions of organosilicon compounds have been known for a long time, one of the early reactions[1] of this type being that in which triethylphenylsilane (itself formed in a sealed tube reaction at 175° from diethylzinc and trichlorophenylsilane) disproportionated into diethyldiphenylsilane and tetraphenylsilane. This disproportionation reaction occurred during either the sealed tube reaction or subsequent manipulations including distillation. It seems likely that the zinc chloride by-product from the original reaction acted as a Lewis acid type catalyst. What may be the first example of the disproportionation of a silicon hydride compound can be found in the silane experiments of Stock and Somieski.[2] During the course of their work, silane and dichlorosilane were allowed to react in a sealed tube with aluminum chloride at 100° for 7 days. Subsequent work-up yielded a significant amount of chlorosilane. No reaction was noted in the cold without added catalyst.

While such disproportionation reactions had been known, it remained for Calingaert, Beatty et al.[3] to establish the identity of the "redistribution reaction," in which random distribution of all possible products is noted. There is ample proof that many such reactions do occur,[3,4,5] but in some cases, such as the methylchlorosilanes[6,7] and the ethoxychlorosilanes,[8] the distribution is nonrandom. As noted previously a disproportionation reaction of a silicon hydride compound has been reported.[2] Other similar reactions are known. For instance, Benkeser, Landesman and Foster[9] in several articles have reported the "apparent redistribution" reactions of phenylsilane and diphenylsilane in the

(1) A. Ladenburg, Ber., 7, 387 (1874). See also, C. Friedel and A. Ladenburg, Ann., 143, 124 (1867), and C. Friedel and J. M. Crafts, Ann. chim. phys., (4) 9, 5 (1866).

(2) A. Stock and C. Somieski, Ber., 52, 719 (1919).

(3) See G. Calingaert and H. A. Beatty in H. Gilman's Organic Chemistry, An Advanced Treatise, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, pp. 1806–20 for a survey of work, including their own, on the redistribution reaction.

(4) H. H. Anderson, J. Am. Chem. Soc., 66, 934 (1944); 72, 2091 (1950); 73, 5800 (1951); G. S. Forbes and H. H. Anderson, J. Am. Chem. Soc., 66, 931 (1944); 67, 1911 (1945).

(5) M. Kumada, J. Inst. Polytech. Osaka City Univ., Ser. C, 2, 131 (1952); [Chem. Abstr., 48, 11303 (1954)].

(6) R. O. Sauer and E. M. Hadsell, J. Am. Chem. Soc., 70, 3590 (1948).

(7) P. D. Zemany and F. P. Price, J. Am. Chem. Soc., 70, 4222 (1948).

(8) M. Kumada, J. Inst. Polytech. Osaka City Univ., Ser. C, 2, 139 (1952); [Chem. Abstr., 48, 11303 (1954)].

(9) R. A. Benkeser, H. Landesman, and D. J. Foster, J. Am. Chem. Soc., 74, 648 (1952); R. A. Benkeser and D. J. Foster, J. Am. Chem. Soc., 74, 4200, 5314 (1952).

TABLE I

DISPROPORTIONATION REACTION OF DIPHENYLSILANE, R_2SiH_2

Run	Reactants[a]	Time, hr.	t, °C.	Products, %[a]
1	R_2SiH_2, $H_2PtCl_6 \cdot 6H_2O$, furan	24[b]	100	Furan, 52; $RSiH_3$, 55.5; R_2SiH_2, 8.2; R_3SiH, 19.3; R_4Si, 0.1
2	R_2SiH_2	24.8[c]	100, 160[c]	R_2SiH_2, 61.3; a mixture[d] (ca. 20%) of R_3SiH and R_2SiH_2 also was obtained
3	R_2SiH_2, $H_2PtCl_6 \cdot 6H_2O$	24.8[c]	100, 160[c]	$RSiH_3$, 73; R_4Si, 15.7
4	R_2SiH_2[e]	13	230[f]	$RSiH_3$, 28.2; R_3SiH, 15.2; R_4Si, 8.1
5	R_2SiH_2, PtO_2[e]	13	230[f]	SiH_4, ?; $RSiH_3$, 26.2; R_2SiH_2, 21; R_3SiH, 10; R_4Si, 7.3
6	R_2SiH_2, Pt[e,g]	13	230[f]	SiH_4, ?; $RSiH_3$, ?
7	R_2SiH_2	3	300[h]	SiH_4, ?; $RSiH_3$, 11.2; R_2SiH_2, 45; R_3SiH, 11.8; R_4Si, 0.1

[a] R stands for C_6H_5. [b] Sealed tube reaction (all others under N_2 gas). [c] Heated first at 100° (24 hr.) then at 160° (8 hr.). [d] The mixture was identified by infrared spectra and n_D^{20}. [e] Reactions 4, 5, and 6 were run simultaneously and a common nitrogen train was used with a single mineral oil bubbler at the outlet. Silane was evolved at this bubbler as evidenced by burning and smoke (smoke identified as SiO_2). Heating 4, 5, and 6 separately indicated that silane was evolved from 5 and 6, but not from 4 (see, however, Reaction 7). [f] Bath temperature. [g] The platinum employed was sheet metal. Dr. Riley Schaeffer identified the silane evolved in this reaction. The gas was collected in a closed flask and later transferred to his vacuum system. When the collecting vessel was removed, a rather violent explosion of some silane remaining in the reaction vessel (ice-cooled) was observed, and the residue was not worked up. The silane sample which was collected melted soon after the liquid nitrogen bath (−196°) was removed and had a vapor pressure of 775 mm. of mercury at −111.9°; silane is reported [A. Stock and C. Somieski, Ber., 49, 111 (1916)] to melt at −186° and to boil at −111.8°. The sample collected also had a trace of liquid which was apparently diphenylsilane (based on an infrared spectrum in carbon disulfide solution). [h] Bath temperature; diphenylsilane would probably boil at ca. 230° at atm. pressure [based on extrapolation of the recorded boiling point (ref. 8) at 0.06 mm. by use of a Pressure-Temperature Alignment Chart].

presence of potassium metal at room temperature or the presence of sodium metal in refluxing decalin. The authors[9] term the reaction "apparent redistribution" because of their theorized mechanism involving cleavage of phenyl groups by the metal, the formation of intermediate phenylsilylmetallic compounds and their subsequent hydrolysis. Such a mechanism is probably quite different from that involved in the use of the usual aluminum chloride type catalyst. However, phenylsilane and phenylmethylsilane have undergone disproportionation reactions in the presence of aluminum chloride.[10] The reactions were carried out at relatively low temperatures (20–50°) and tended to explode in the presence of atmospheric oxygen. Ether completely retards this reaction. The same authors[10] also report the disproportionation of phenylmethylsilane and of chlorophenylsilane using an aluminum chloride catalyst.

Most of the disproportionation or redistribution reactions of organosilicon compounds have been catalyzed by aluminum chloride[2,3,10−12] or related compounds (e.g., zinc chloride in the sealed tube reaction mentioned previously[1]), or have had halosilanes present which may act as the catalyst.

A recent series of patents[13] describes the catalysis of such reactions with alkali metal alkoxides. Some silicon hydride compounds are among those so disproportionated. In other recent work it has been shown[14] that alkylaluminum hydride compounds and silicon tetrahalides redistribute the hydrogen and halogen to give silicon hydride compounds rather than silicon alkyl compounds.

We now wish to report that diphenylsilane undergoes a disproportionation reaction in the presence of a platinum catalyst or in the absence of any added catalyst. The initial discovery was made during an attempt to add diphenylsilane to furan using chloroplatinic acid as the catalyst. The use of this catalyst for similar addition reactions has been recommended by Speier, Webster, and Barnes.[15] The original reaction was carried out in a sealed tube heated at 100° for 24 hr. Work-up of the reaction mixture, which originally contained 0.1 mole each of furan and diphenylsilane with a small amount of catalyst, yielded 52% of the furan, 8.2% of the diphenylsilane, 55.5% of phenylsilane, 19.3% of triphenylsilane, and 0.1% of tetraphenylsilane. A series of experiments, summarized in Table I, was carried out to establish whether chloroplatinic acid or another platinum catalyst, furan, or simply

(10) J. L. Speier and R. E. Zimmerman, J. Am. Chem. Soc., 77, 6395 (1955).

(11) P. D. George, L. H. Sommer, and F. C. Whitmore, J. Am. Chem. Soc., 77, 1677 (1955).

(12) R. O. Sauer (to General Electric Co., Inc.) U. S. Patent 2,730,983, Jan. 10, 1956; [Chem. Abstr., 50, 12108 (1956)].

(13) D. L. Bailey (to Union Carbide and Carbon Co., Inc.) U. S. Patent 2,723,983; 2,723,984; 2,723,985; Nov. 15, 1955; [Chem. Abstr., 50, 10125 (1956)].

(14) R. Köster, Angew. Chem., 68, 383 (1956).

(15) J. L. Speier, J. A. Webster, and G. H. Barnes, J. Am. Chem. Soc., 79, 974 (1957).

heat would cause the reaction. Comparison of Runs 4 and 5 indicates that there is no substantial difference in reactions containing catalyst and those not containing catalyst at this temperature (230°), although no silane gas was noted in the noncatalyzed reaction. At the lower temperature of Runs 2 and 3, the platinum definitely seems to act as a catalyst. Comparison of Runs 2, 4, and 7 shows that *increased temperature will cause disproportionation of diphenylsilane in the absence of any added catalyst.*

The fact that such disproportionations occur should be of interest in view of current research with regard to the addition reactions of silicon hydride compounds; these important side reactions may be caused by certain catalysts or take place in the absence of any added catalyst.

It would be interesting to consider whether many other substances may redistribute in the absence of added catalyst, provided that their decomposition temperatures are not too low.

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Stereoselectivity in the Carbanion-Catalyzed Isomerization of 1-Butene[1]

Sir:

The double bond isomerization of alkenes and cyclenes in the presence of a sodium catalyst has been reported recently,[2-4] and it was observed[3a,b] that this is a reversible reaction leading to an equilibrium mixture.

It was suggested that the double bond migration occurs through a chain mechanism involving a carbanion attack on an allylic hydrogen. In order

(1) Paper XII of the series "Base Catalyzed Reactions of Hydrocarbons." For paper XI see M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, 79, 5820 (1957).

(2) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, 77, 347 (1955).

(3) H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, (a) 77, 6314 (1955); (b) 78, 1178 (1956); (c) 78, 5950 (1956).

(4) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, 20, 839 (1955).

to elucidate further the mechanism of double bond migration a kinetic study of the carbanion-catalyzed isomerization of alkenes was undertaken.

The present communication deals with the isomerization of 1-butene to 2-butenes in the temperature range of 37–195° using as catalysts sodiumanthracene, sodium-alumina, and lithium-alumina.

It was found that the initial products obtained from the isomerization of 1-butene over a sodiumanthracene catalyst are kinetically controlled and that the less stable cis-2-butene is produced at a higher rate than the trans isomer. The initial ratio of the cis/trans isomers decreases with increasing temperature, as indicated in Table I.

TABLE I

RESULTS OBTAINED FROM THE ISOMERIZATION OF 1-BUTENE[a]

Time, Min.	Butene %			cis/trans[a]
	1-	2-trans	2-cis	
Temperature 145°				
10	95.9	1.4	2.7	2.0
40	86.6	4.5	8.9	2.0
70	71.5	9.6	18.9	2.0
160	20.0	30.9	49.1	1.6
Temperature 195°				
10	87.4	5.7	6.9	1.20
25	74.5	11.8	13.7	1.16
45	55.5	21.4	23.1	1.1
65	39.9	31.0	29.1	0.94
105	22.3	46.5	31.2	0.67
145	18.1	50.4	31.5	0.63
245	14.7	54.4	30.9	0.57
Calcd.[b]	12.6	58.3	29.1	0.50

[a] The reaction was carried out in a 450-ml. capacity rotating autoclave charged with 5 g. of 1-butene, about 1 g. of sodium and 0.4 g. of anthracene. [b] Calculated from the thermodynamic data.[6]

When the sodium is dispersed on powdered alumina[5] it is possible to carry out the isomeriza-
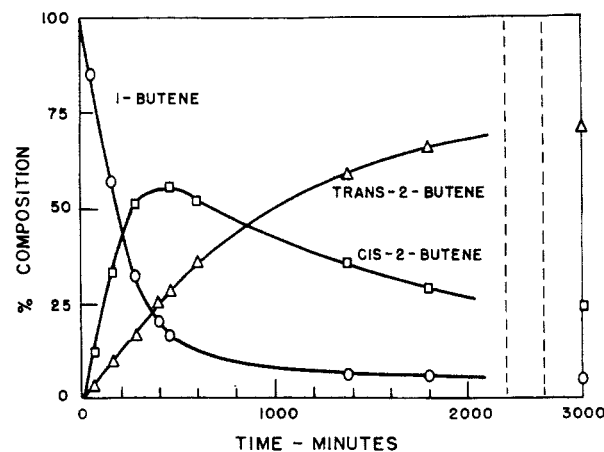

Fig. 1. Isomerization of 1-Butene. The reaction was made in a 450 ml. autoclave at 37° using 20 g. of 8% sodium on alumina and 16 g. of 1-butene

(5) S. E. Voltz, *J. Phys. Chem.*, 61, 756 (1957).