mm., n_{D}^{20} 1.5139, d_4^{20} 0.919, lit. b.p. 191° (atm.),[13] n_{D}^{20} 1.5141[14]). The infrared spectrum of V was consistent with its structure and possessed the doublet at 7.27 μ and 7.38 μ due to the *gem*-dimethyl grouping. V was free of contaminants in vapor phase chromatography (retention time of 7 min., 160°, Perkin-Elmer silicone oil column "O").

2-Methyltetralin (VI). Tetralone-1 (14.6 g., 0.1 mole) was converted[15] to its 2-hydroxymethylene derivative[16] (14.6 g., 84%, b.p. 147° at 4 mm., n_{D}^{20} 1.6339, lit.[16] b.p. 105–107° at 1 mm., n_{D}^{19} 1.6341). This derivative (12.3 g., 0.071 mole) was then alkylated with methyl iodide (20.2 g., 0.124 mole), using the technique reported for the 6-methoxy analog,[17] which employs sodium amide in dimethylformamide as the base, to give 2-methyltetralone-1 (4.3 g., 39%, b.p. 115° at 10 mm., n_{D}^{20} 1.5544, 2,4-dinitrophenylhydrazone m.p. 224°, lit.[18] b.p. 126° at 12.5 mm., n_{D}^{20} 1.5541, 2,4-dinitrophenylhydrazone m.p. 224°). Catalytic hydrogenolysis (40 p.s.i.) of this ketone (3.6 g., 0.023 mole) in methanol (20 ml.) and sulfuric acid (0.25 g.) over palladium-on-carbon (10%, 0.25 g.), as described for V above, led to VI (2.2 g., 67%, b.p. 222° (atm.), n_{D}^{20} 1.5261, lit.[18] b.p. 219.8° at 751 mm., n_{D}^{20} 1.5267, d_4^{20} 0.9432). The infrared spectrum of VI was consistent with its structure. VI possessed at 160° retention times of 12.5 min. ("O" column above) and 24 min. (Perkin-Elmer didecyl phthalate "A" column). A trace contaminant (< 0.5%) was neglected in the subsequent use of VI.

Decarbonylation studies. The technique employed was that used earlier,[2] except that no distillation of the reaction material was performed. Rather, when gas evolution ceased or at various known times, measured aliquots of the material were withdrawn through a small side neck of the flask capped with a rubber septum and analyzed by vapor phase chromatography for V and VI through comparison with standards. The ratio of areas method was used. The following are, for each *experiment*, the mmoles of IV, mmoles of di-*t*-butyl peroxide, total reaction time (min.), carbon monoxide evolved (%), and *rearrangement* (%): *1*, 14, 3.1, 400, 89, *35*; *2*, 11.5, 23, 495, 89, *33*; *3*, 13.7, 82, 360, 89, *46*; *4*, 9.9, 2, 400, 81, *35*; *5*, 9.5, 0.95, 395, not determined, *34*. The bath temperature for all experiments was 160° and the yield of V and VI was 76% in experiment 4 and 81% in experiment 3. The di-*t*-butyl peroxide was 10 mole percent initially in experiments 1 and 4, with the additional amount being added at 340 and 120 min., respectively.

Attempted isomerization of V. V (0.25 g., 1.71 mmoles) and di-*t*-butyl peroxide (0.025 g., 0.17 mmole) were heated at 160° (bath) for 8 hr., the time of the longest decarbonylation study. Analysis by vapor phase chromatography showed but a trace of product other than V. Likewise, a completed decarbonylation reaction residue (65% V, 35% VI) was again heated under the above conditions with a small quantity of added di-*t*-butyl peroxide and IV for 100 min. The ratio of V and VI at the end of this time was unchanged (vapor phase chromatography).

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(13) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934).

(14) L. Schaap and H. Pines, *J. Am. Chem. Soc.*, **79**, 4967 (1957).

(15) W. S. Johnson and H. Posvic, *J. Am. Chem. Soc.*, **69**, 1363 (1947).

(16) E. Ott and D. S. Tarbell, *J. Am. Chem. Soc.*, **74**, 6266 (1952).

(17) N. A. Nelson, J. C. Wollensak, R. L. Foltz, J. B. Hester, Jr., J. I. Brauman, R. B. Garland, and G. H. Rasmussen, *J. Am. Chem. Soc.*, **82**, 2569 (1960).

(18) A. S. Bailey and C. M. Staveley, *J. Inst. Petroleum*, **42**, 97 (1956), *Chem. Abstr.*, **51**, 6572f (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Unrearranged Elimination and Substitution Products from 2,2-Diphenylethyl Tosylate with Bases. Rearrangement with Acidic Reagents[1]

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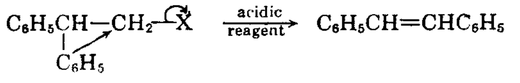
2,2-Diphenylethyl tosylate underwent rearrangement with acidic reagents to form stilbene, but produced unrearranged elimination and/or substitution products with basic reagents. The reactions with alkali amides in liquid ammonia and with alkali methoxides in refluxing methanol gave exclusively 1,1-diphenylethylene, whereas those with piperidine and morpholine yielded largely the corresponding tertiary amines. Certain other basic reagents produced both elimination and substitution products.

Acidic reagents effect the elimination of HX from alcohol (I) and its tosylate or halide (II) accompanied by rearrangement to form stilbene. Presumably these reagents coordinate with a free pair of electrons on X to promote its ionization and the shift of a phenyl group (Equation 1).



$$C_6H_5\underset{\underset{C_6H_5}{|}}{C}H\!-\!CH_2\!-\!X \xrightarrow[\text{reagent}]{\text{acidic}} C_6H_5CH{=}CHC_6H_5 \qquad (1)$$

I. X = OH
II. X = OTs, Cl, or Br

Earlier workers have obtained stilbene from alcohol (I) on dehydration with phosphorus pentoxide in refluxing benzene,[3,4] and from tosylate (II) on heating in glacial acetic acid.[5] A kinetic study of the latter reaction afforded evidence for participation of the phenyl group in the ionization of X and the rearrangement.[5]

We have isolated stilbene in high yields on treatment of alcohol I with hydrogen bromide or phos-

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[1] Supported by the National Science Foundation.

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(3) P. Ramart and P. Amagat, *Ann. chim.*, [10] **8**, 263 (1927).

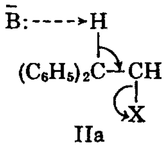
(4) M. S. Kharasch and H. G. Clapp, *J. Org. Chem.*, **3**, 257 (1938).

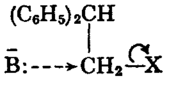
(5) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

phorus tribromide under conditions that generally convert alcohols to the corresponding bromides. Apparently pure halide (II) has never been prepared, at least not from alcohol (I).

Even heat alone may bring about the rearrangement of II. Thus, Hepp[6] reported that crude chloride (II), prepared from chlorodiethyl acetal and benzene by means of sulfuric acid, yielded stilbene on attempted distillation. We have obtained stilbene on heating tosylate (II) above its melting point.

In spite of this inherent tendency to rearrange, however, tosylate or halide (II) might be expected to react with bases or nucleophilic reagents to produce unrearranged elimination or substitution products. This is because these reagents may attack the β-hydrogen or α-carbon as indicated in IIa and IIb, respectively.[7]


IIa


IIb

In agreement with this, Hepp[6] reported that crude chloride (II) reacted with ethanolic sodium ethoxide to form the unrearranged olefin, 2,2-diphenylethylene, though no yields were given.

We have found that tosylate (II) reacts with various basic reagents to form unrearranged elimination or substitution products (Table I). Tosylate (II) was readily prepared in the pure condition from the sodio or potassio salt of alcohol (I) and *p*-toluenesulfonyl chloride in ether, the alcohol (I) being obtained by two routes (Scheme A). The direct method involving potassium diphenylmethide and formaldehyde, followed by tosyl chloride, is considered the more convenient.

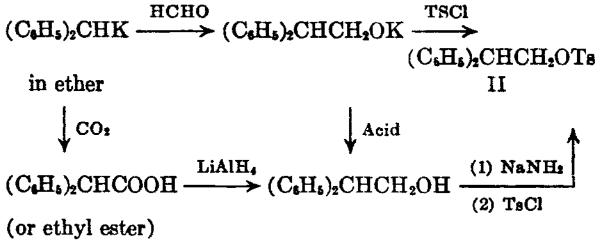


TABLE I

UNREARRANGED ELIMINATION AND SUBSTITUTION PRODUCTS FROM TOSYLATE II WITH BASIC REAGENTS

Expt. No.	Basic Reagent	Solvent (Reflux)	Elimination Product Yield, %	Substitution Product Yield, %
1	KNH_2	Liq. NH_3	90	0
2	$LiNH_2$	Liq. NH_3	94	0
3	CH_3OK	CH_3OH	87	0
4	CH_3ONa	CH_3OH	91[a]	0
5	CH_3OLi	CH_3OH	92[a]	0
6	$(C_2H_5)_2NMgBr$	Ether	86[b]	12
7	$(C_6H_5)_2CHNa$	Liq. NH_3	62[a]	16[a]
8	Piperidine	Piperidine[c]	—[d]	59
9	Morpholine	Morpholine[c]	—[d]	65

[a] Yield based on tosylate used minus that recovered. [b] A polymer was obtained, the yield being calculated as unrearranged olefin III. [c] Steam bath temperature. [d] A small amount of unrearranged olefin III appeared to be formed.

Tosylate (II) reacted with alkali amides in liquid ammonia (expts. 1 and 2, Table I) and with alkali methoxides in refluxing methanol (expts. 3-5) to form exclusively the unrearranged olefin (III) (Equation 2).

$$\text{II} \xrightarrow[\text{or } MOCH_3(CH_3OH)]{MNH_2\ (\text{liq. } NH_3)} (C_6H_5)_2C{=}CH_2 \qquad (2)$$

Not only was the olefin (III) isolated in excellent yields (87–94%) and some polymer of III also obtained in certain cases, but no stilbene was found. Blank experiments with III and stilbene indicated that as little as 5% of stilbene could have been isolated had it been presented. Moreover the ultraviolet absorption spectrum of the crude product from the reaction with potassium methoxide was identical with that of an authentic sample of III prepared by the dehydration of 1,1-diphenylethanol with sulfuric acid.[8]

The reactions of tosylate (II) with the alkali amides (see Equation 2) are of particular interest, since they were accompanied by the immediate production of red colors that faded as the reactions proceeded. These observations may indicate that the β-hydrogen is first ionized to form the benzohydryl type of carbanion (II′), which then undergoes β-elimination of the tosylate anion. However,

$$\underset{\text{II}'}{(C_6H_5)_2\bar{C}{-}CH_2OTs}$$

the intermediate formation of this carbanion cannot be considered established, since a red color was also produced on subsequently treating olefin III with potassium amide in liquid ammonia, under which condition a yellow polymer was obtained. The red intermediate in this polymerization was presumably IIIa, which is similar to that proposed in the amide ion catalyzed polymerization of styrene.[9]

$$\underset{\text{IIIa}}{(C_6H_5)_2\bar{C}{-}CH_2NH_2}$$

Since the reactions of tosylate (II) with the alkali methoxides (see Equation 2) were not accompanied by observable colors, they may be considered to

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[6] E. Hepp, *Ber.*, **7**, 1409 (1874).

[7] See C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 933 (1940).

[8] C. F. H. Allen and S. Converse, *Org. Syntheses*, Coll. Vol. II, 221 (1932).

[9] J. J. Sanderson and C. R. Hauser, *J. Am. Chem. Soc.*, **71**, 1595 (1949); W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, 760, 1178 (1952).

involve the usual E2 mechanism indicated by IIa in which the proton and OTs group are removed simultaneously. Actually Burr[10] has shown that the reaction (in Methyl Cellosolve) follows second order kinetics, although he did not determine by product analysis whether it involved elimination or substitution.

Tosylate (II) reacted with diethylaminomagnesium bromide in refluxing ether (expt. 6, Table I) to form mainly a polymer and some (12%) of the unrearranged substitution product (IV). The latter product might possibly have been formed from reaction of II with unchanged diethylamine, which was employed in the preparation of the reagent. Such a reaction was observed with certain other secondary amines at a higher temperature (see below).

$$(C_6H_5)_2CHCH_2N(C_2H_5)_2$$

IV

The polymer arose presumably from the unrearranged olefin (III), not from stilbene, since only the former olefin yielded such a polymer under similar conditions. The structure of the substitution product was established as IV by an independent synthesis (Equation 3), the Grignard reagent being prepared from potassium diphenylmethide and magnesium bromide[11] instead of in the usual manner.

$$(C_6H_5)_2CHMgBr \xrightarrow{C_2H_5OCH_2N(C_2H_5)_2} IV \qquad (3)$$

Tosylate (II) reacted with sodium diphenylmethide in liquid ammonia (expt. 7, Table I) to form mainly unrearranged olefin (III), (77%) but some (16%) of the unrearranged substitution product (V) was also obtained.

$$(C_6H_5)_2CHCH_2CH(C_6H_5)_2$$

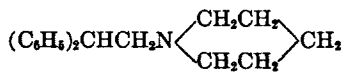
V

The structure of this hydrocarbon was established by an independent synthesis from sodium diphenylmethide and methylene chloride (Equation 4).[12]

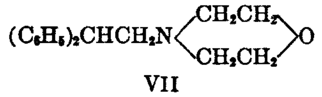
$$2(C_6H_5)_2CHNa \xrightarrow[\text{liq. } NH_3]{CH_2Cl_2} V \qquad (4)$$

Recently[13] α,β-diphenylethyl chloride, which has a less reactive β-hydrogen than II, was observed to undergo mainly the substitution type of reaction with sodium diphenylmethide in liquid ammonia even though the more weakly basic sodium ethoxide effected largely β-elimination under similar conditions.

Tosylate (II) reacted with excess piperidine (expt. 8, Table I) and with excess morpholine (expt. 9) to form the corresponding unrearranged substitution products (VI and VII) in yields of 59 and 65%, respectively. Small amounts of the unrearranged olefin III also appeared to be produced but no stilbene was found.



VI



VII

The structures of these tertiary amines were established as VI and VII, respectively, by independent syntheses from benzohydrylmagnesium bromide and the appropriate α-amino ether by reactions analogous to that represented by Equation 3.

The fact that II underwent mainly substitution with the secondary amines is interesting, since not only is the β-hydrogen activated by two phenyl groups but the reaction was effected on the steam bath, the relatively high temperature of which might have been expected to lead to β-elimination. The result may be ascribed to the weakly basic nature of the secondary amines, since II exhibited exclusively β-elimination with the more strongly basic amide and methoxide ions even at much lower temperatures.

Rather surprisingly, tosylate (II) failed to react appreciably with phenyllithium or phenylmagnesium bromide in refluxing ether during twelve hours, after which 80–90% of the tosylate was recovered.

It should be mentioned that the related bromides (VIII) have previously been shown[14] to react with potassium amide in liquid ammonia to form largely the corresponding unrearranged olefins (IX).

$$\underset{R}{C_6H_5CH}{-}CH_2Br \qquad \underset{R}{C_6H_5C}{=}CH_2$$

VIII, R = CH_3 or C_2H_5. IX, R = CH_3 or C_2H_5.

A little of the rearranged olefin was also obtained but it presumably arose from rearranged bromide formed in the preparation of VIII from the corresponding alcohol and phosphorus tribromide.[14]

EXPERIMENTAL[15]

2,2-Diphenylethanol (I). *Method A.* An ethereal suspension of potassium diphenylmethide (0.3 mole) was prepared from 0.3 mole each of diphenylmethane and potassium amide in liquid ammonia, the ammonia being replaced by ether.[16] Gaseous formaldehyde (from dried paraformaldehyde) was passed into the stirred suspension until the red color of the

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[10] J. G. Burr, *J. Am. Chem. Soc.*, **75**, 5008 (1953).

[11] C. R. Hauser and D. S. Hoffenberg, *J. Am. Chem. Soc.*, **77**, 5742 (1955).

[12] C. R. Hauser, C. F. Hauser, and P. J. Hamrick, Jr., *J. Org. Chem.*, 24, 397 (1959).

[13] C. R. Hauser, C. F. Hauser, and P. J. Hamrick, Jr., *J. Org. Chem.* 23, 1713 (1958).

[14] C. R. Hauser, P. S. Skell, R. D. Bright, and W. B. Renfrow, *J. Am. Chem. Soc.*, **69**, 589 (1947).

[15] Melting points are uncorrected. Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[16] R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, 69, 2325 (1947).

reagent was discharged. The resulting gray suspension was shaken with dilute hydrochloric acid, and the two layers were separated. The ethereal layer, combined with an ethereal extraction of the aqueous layer, was dried over magnesium sulfate. After filtering, the solvent was removed, and the residue was distilled *in vacuo* to give a small forerun of diphenylmethane and 48 g. (81%, based on diphenylmethane) of clear, colorless 2,2-diphenylethanol (I), b.p. 150–151° at 3 mm. which solidified on standing, m.p. 57–58°; reported m.p. 59.1–59.5°.[5]

Method B. Ethyl diphenylacetate was prepared by carbonation of potassium diphenylmethide, followed by esterification as described previously.[5] The ester (0.3 mole) was reduced with lithium aluminum hydride (0.6 mole) in ether. After adding 10 ml. of ethyl acetate to destroy any unchanged hydride, the reaction mixture was shaken with 300 ml. of a saturated solution of ammonium chloride. There was obtained alcohol (I) in 93% yield (based on the ethyl diphenylacetate), m.p. 58–59°.

Diphenylacetic acid has previously been reduced with lithium aluminum hydride in 84% yield.[5]

Reaction of alcohol (I) *with acidic reagents.* (*A*) *With hydrogen bromide.* This reaction was carried out at 100° essentially described previously[17] for the conversion of *n*-dodecyl alcohol to its bromide. There was obtained from 28 g. (0.141 mole) of I, 23 g. (92%) of stilbene, m.p. 121–122°. This melting point was not depressed on admixture with an authentic sample of stilbene (m.p. 122°).

(*B*) *With phosphorus tribromide.* To a solution of 19.8 g. (0.1 mole) of alcohol I in 100 ml. of benzene was added with stirring a solution of 9.1 g. of phosphorus tribromide in 50 ml. of benzene. After standing overnight at room temperature, the reaction mixture was shaken with 50 ml. of cold water, and the two layers were separated. The benzene layer was dried over magnesium sulfate. After filtering and reducing the volume of the benzene solution to about 50 ml., petroleum ether (b.p. 30–60°) was added to precipitate, on cooling, 17 g. (94%) of stilbene, m.p. 121–122°. This melting point was not depressed on admixture with an authentic sample of stilbene.

2,2-Diphenylethyl tosylate (II). To an ethereal suspension of the potassium salt of alcohol (I), prepared from 0.3 mole of potassium diphenylmethide and excess formaldehyde as described above under Method A, was added with stirring a solution of 0.3 mole of *p*-toluenesulfonyl chloride in 250 ml. of ether. After stirring for 2 hr., the reaction mixture was shaken with water to dissolve the potassium chloride. The solid tosylate that remained was collected on a funnel, and washed with water. More of this compound was obtained on evaporation of the ethereal layer of the filtrate. The combined product was recrystallized from acetone to give a 69% yield (based on diphenylmethane) of long, white needles of tosylate (II), m.p. 117–118°; reported m.p. 116°.[4]

Anal. Calcd. for $C_{21}H_{20}SO_3$: C, 71.36; H, 5.70. Found: C, 71.62; H, 5.53.

Tosylate (II) was also prepared from alcohol (I), obtained by either Method A or B described above, by converting this alcohol to its sodium salt by metallic sodium in ether or by sodium amide in liquid ammonia, the ammonia being replaced by ether. To the ethereal suspension of the sodium alcoholate was added an equivalent amount of *p*-toluenesulfonyl chloride in ether. The resulting reaction mixture was worked up to give an 85% yield [based on alcohol (I)] of tosylate (II), m.p. 117–118°.

Thermal rearrangement of tosylate (II). A 3-g. sample of tosylate (II) was fused in a test tube in a Wood's Metal bath for 10 min. The resulting brown mass was triturated with water and the solid filtered from the solution. The solid was dissolved in ethanol and the solution treated with decolorizing carbon. Evaporation of the filtered solution deposited stilbene, m.p. 122°.

Reactions of tosylate (II) *with basic reagents* (*Table I*). (*A*) *With alkali amides.* To a stirred solution of 0.0142 mole of potassium amide in 150 ml. of liquid ammonia was added 5 g. (0.0142 mole) of tosylate (II) to produce immediately a red color that faded as reaction progressed. After 2 hr. when the reaction mixture was only slightly pink, 2 g. of solid ammonium chloride was added, and the ammonia replaced by ether. Water was added, and the two layers were separated. The ethereal layer (with which was combined an ethereal extract of the aqueous layer) was dried over magnesium sulfate. After filtering, the solvent was removed, and the residue was distilled *in vacuo* to give 2.3 g. (90%) of 1,1-diphenylethylene (III), b.p. 139–140° at 11 mm.

Similarly tosylate (II) (0.0142 mole) was added to lithium amide (0.0142 mole) in liquid ammonia to produce a reddish color that faded within about 1 hr. The reaction mixture was neutralized with ammonium chloride to give 2.4 g. (94%) of 1,1-diphenylethylene (III), b.p. 139–140° at 11 mm.

The olefin was identified by treatment with bromine in carbon disulfide (steam bath) until hydrogen bromide ceased to be evolved. The product was crystallized from aqueous-ethanol to give crystals of 2,2-diphenylvinyl bromide, m.p. 51–52°; reported m.p. 50.[6]

In an inverse addition procedure, a solution of 0.014 mole of potassium amide in 200 ml. of liquid ammonia was added to a suspension of 5 g. (0.0142 mole) of tosylate (II) in 100 ml. each of liquid ammonia and ether. A few milliliters of the amide solution produced a red color that faded when the addition was stopped. When all the amide solution had been added the red color persisted for 5 min., after which time the ammonia was evaporated (steam bath). The remaining ether suspension was shaken with water and the two layers were separated. The ether layer was combined with two ether extracts of the aqueous layer. The ether solution was dried over magnesium sulfate and the solvent removed. The residue afforded 0.5 g. of recovered tosylate (II), m.p. 116,° and a liquid, which was distilled to give olefin (III), b.p. 134–140° at 10 mm., some yellow polymer remaining in the flask. The infrared spectrum of the olefin was identical with that of an authentic sample of III.[8]

(*B*) *With alkali methoxides.* To solutions of 0.0142 mole of potassium, sodium, or lithium methoxides in 100 ml. of absolute methanol (prepared by adding the alkali metal to the alcohol) was added 5 g. (0.0142 mole) of tosylate (II). The resulting solution was refluxed for 24 hr. After cooling and evaporating most of the methanol under suction, aqueous ammonium chloride was added, and the mixture was extracted twice with ether. The combined ethereal solution was dried over magnesium sulfate and filtered. The solvent was removed from the filtrate, and the residue was distilled *in vacuo* to give 1,1-diphenylethylene, b.p. 139–140° at 11 mm. in yields of 87–92%. A little of II was recovered in the experiments with sodium and lithium methoxides (see note a of Table I).

(*C*) *With diethylaminomagnewium bromide.* To a stirred solution of 0.03 mole of ethylmagnesium bromide in 100 ml. of ether cooled in an ice bath was added 1.32 g. (0.03 mole) of diethylamine in 50 ml. of dry ether. After 0.5 hr., the ice bath was removed, and 10 g. (0.0284 mole) of tosylate (II) was added. The reaction mixture was stirred overnight and then neutralized with aqueous ammonium chloride solution. The two layers were separated. The ether layer was dried over Drierite, and the solvent was removed. The residue was distilled *in vacuo* in the presence of a little hydroquinone to give 0.9 g. (12%) of amine (IV), b.p. 172° at 11 mm., leaving a clear yellow polymer (see Table I). Such a polymer was produced when the olefin (III) was treated with diethylaminomagnesium bromide under these conditions, whereas stilbene was recovered after similar treatment.

Independent synthesis of amine (IV) was effected by treating 0.3 mole of benzohydrylmagnesium bromide[11] in 1 l.

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(17) E. E. Reid, J. R. Ruhoff, and R. E. Burnett, *Org. Syntheses*, **15**, 24 (1935).

of ether with 47.7 g. (0.3 mole) of *n*-butyl *N*,*N*-diethylaminomethyl ether[18] in 200 ml. of dry ether. After 1 hr. the reaction mixture was decomposed with water, and the two layers were separated. The ether layer was dried over magnesium sulfate and the solvent removed. The residue was distilled *in vacuo*, the fraction boiling at 140–165° at 8 mm. being collected. Redistillation of this fraction gave 32.4 g. (43%) of amine IV, b.p. 171–171.5° at 10 mm.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.54. Found: C, 85.53; H, 9.17; N, 5.35.

Samples of amine (IV) obtained by each method were converted to the picrate which, after recrystallization from ethanol, melted at 192–193°; a mixture melting point was the same.

(*D*) *With sodium diphenylmethide.* To a stirred solution of 0.03 mole of sodium diphenylmethide in 300 ml. of liquid ammonia[12] was added 10 g. (0.0285 mole) of tosylate (II). After 3 hr. (red color of reagent discharged), the ammonia was evaporated as an equal volume of ether was added. The resulting suspension was shaken with water, and the two layers were separated. The ether layer was dried over Drierite, and the solvent was partly removed to precipitate unchanged tosylate (II), which was removed by filtration (3 g. of II, m.p. 116°, after recrystallization from acetone). The ether filtrate was evaporated almost to dryness, and petroleum ether (b.p. 30–60°) was added. The resulting mixture was cooled in a Dry Ice–acetone bath to precipitate hydrocarbon (V), which was removed by filtration (1.2 g. of V, m.p. 80–81° after recrystallization from ethanol; its infrared spectrum was identical with that of an authentic sample of V[12]). The filtrate was distilled to give 2.75 g. of olefin (III), b.p. 137–140° at 11 mm. (see note a of Table I), contaminated with about 15% of diphenylmethane as estimated from the infrared absorption spectrum.

(*E*) *With piperidine.* A solution of 3.0 g. of tosylate (II) in 50 ml. of piperidine was heated on the steam bath for 6 hr. Excess amine was removed under reduced pressure, and the residue was taken up in ether. After washing with water, the ether solution was dried over Drierite, and the solvent removed. The residue was dissolved in 50 ml. of ethanol, and the solution treated with 50 ml. of saturated picric acid solution diluted with 80 ml. of ethanol. Overnight standing afforded large yellow crystals, which were recrystallized from ethanol to give 2.9 g. (59%) of the picrate of *N*-(2,2-diphenylethyl)piperidine (VI), m.p. 186°.

Anal. Calcd. for $C_{25}H_{26}N_4O$: C, 60.72; H, 5.30; N, 11.33. Found: C, 61.11; H, 5.50; N, 11.23.

Independent synthesis of VI was effected[19] by treating 0.15 mole of benzohydrylmagnesium bromide[11] in 300 ml. of ether with 20.5 g. (0.12 mole) of *N*-*n*-butoxymethylpiperidine[18] (b.p. 72–73.5° at 3.5–4 mm., $n_D^{23.5}$ 1.4454, yield 66%) in 100 ml. of ether. After 16 hr. at room temperature, the reaction mixture was decomposed with hydrochloric acid and the resulting two phases made basic with ammonium hydroxide. The layers were separated. The solvent was removed from the ether layer, and the residue distilled to give 16.3 g. (51%) of amine (VI), b.p. 118–120° at 0.12 mm., n_D^{24} 1.5663 (lit. b.p. 167–170° at 1 mm.).[20] The picrate melted at 184–185; this melting point was not depressed on admixture with a sample of the picrate obtained as described above.

(*F*) *With morpholine.* A solution of 3.0 g. of tosylate II in 50 ml. of morpholine was heated on the steam bath for 4 hr., and then allowed to stand overnight at room temperature. The reaction mixture was worked up as described above for that with piperidine. There was obtained 3.2 g. (65%) of the picrate of *N*-(2,2-diphenylethyl)morpholine (VII), m.p. 206–207° after recrystallization from ethanol.

Independent synthesis of amine (VII) was effected[19] from benzohydrylmagnesium bromide and *N*-*n*-butoxymethylmorpholine (b.p. 75–76° at 2.4 mm., n_D^{25} 1.4442, yield 54%) essentially as described above for the amine (VI). There was obtained 17.1 g. (53%) of amine (VII), m.p. 50–51° (recrystallized from ligroin, b.p. 60–90°).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.21; H, 8.05; N, 5.20.

The picrate melted at 205–207°, which was not depressed on admixture with a sample of the picrate obtained as described above.

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(19) We are indebted to Dr. G. F. Morris for performing this experiment.

(20) O. Exner, J. Pliml, and M. Protiva, *Chem. Listy*, 48, 65 (1954).

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Decomposition of Ditriphenylmethyl Peroxide in Concentrated Sulfuric Acid

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Gomberg's early work on the decomposition of ditriphenylmethyl peroxide in concentrated sulfuric acid has been repeated and confirmed. Evidence is presented for the mechanism whereby the major product is triphenylcarbinol. The base soluble products are shown to result from the oxidation of triphenylcarbonium ion by Caro's acid.

In several of Gomberg's early papers on triphenylmethyl[1,2] it was reported that on diluting ditriphenylmethyl peroxide dissolved in cold concentrated sulfuric acid with water an 80% yield of triphenylcarbinol was obtained. This observation was found to be disturbing for several reasons. First of all it appeared on first glance to be a reduction taking place in concentrated sulfuric acid. Secondly, a likely mechanism which involved the protonation of one of the peroxide oxygens followed by a heterolytic oxygen–oxygen cleavage should have given rise to triphenylcarbinol and a triphenylmethoxy cation. The triphenylmethoxy cation would be expected to undergo a 1,2-rearrangement whereby a phenyl group migrates to the oxygen atom with the open sextet. Such rearrangements have been postulated for the Baeyer-Villiger

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(1) M. Gomberg, *Chem. Ber.*, 33, 3157 (1900).

(2) M. Gomberg, *J. Am. Chem. Soc.*, 22, 765 (1900).