melted at 65.2–67.2°. Chemical analysis showed only a trace of sulfur. The material was recrystallized from boiling heptane several times to a constant melting point of 75.5–76.0°. This agrees with the reported[3] value for perfluorodicyclohexyl. This compound was analysed by vapor phase chromatography using the fluorocarbon resin column and appeared to be 99% one component. The infrared spectrum of a melt agreed exactly with that for perfluorodicyclohexyl as determined by Tatlow.[3] The carbon and fluorine analyses of the compound were within 0.3% of the calculated values.

A final fraction was isolated at 126° and 37 mm. This was a slush amounting to only 12 g. Six grams of crude filtration residue melted at 65–67.5°. It decomposed at 180 to 200° and accordingly could not be analysed by vapor phase chromatography. At lower temperatures the development time was so long that only one broad low peak was obtained. Consequently, the material was recrystallized from hot heptane to a constant melting point of 90–91°. Analysis and molecular weight by the cryoscopic method in Freon 112 indicated that the purified material was the perfluorodicyclohexylsulphur tetrafluoride, $(C_6F_{11})_2SF_4$, mol. wt. 670; observed mol. wt. 660, m.p. 90–91°.

Anal. Calcd. for $C_{12}F_{26}S$: F, 73.73; S, 4.77. Found: F, 73.38; S, 4.81.

In both of the reported operations considerable material boiling well above the highest boiling products reported was obtained. This is not uncommon in low voltage electrolyses in hydrogen fluoride.

Better yields of the cyclic derivatives would probably have been obtained if the starting sulfide had been the cyclohexyl sulfide instead of the phenyl derivative. Further evidence for this statement is apparent from the fact that, in general, unsaturated compounds even though resonance stabilized tend to run poorly in the cells and frequently cause corrosion of the electrodes. Although the corrosion in this case was not as severe as that generally encountered with unsaturated materials, nickel bearing compounds were found in the cell in some quantity. Furthermore, they were observed to react with water quite violently with the evolution of heat and sparks.

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The Interaction of Some Arylamines with Dowex-50 in 1,2-Dimethoxyethane

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The use of ion exchange resins has been largely limited to aqueous solutions or polar solvents. To a certain extent this is because of the generally higher degree of resin swelling than that which occurs in nonpolar solvents. It is not necessary for a resin to swell in order to exhibit an appreciable ion exchange capacity. However, swelling helps to accommodate larger exchanging particles (molecules or ions).[1] Many organic compounds show limited solubilities in polar solvents or react with them. Studies show that Dowex-50 is effective in removing various aromatic amines from a solution of the amine in anhydrous 1,2-dimethoxyethane.[2] The degree of swelling of the ion exchange resin is, as might be expected, a function not only of the solvent but also of the extent to which the resin is crosslinked. The rate of adsorption of the amine is a function of the steric requirements of the amine as well as the degree of swelling and hence the porosity of the resin. By selectively swelling the ion exchange resin it is possible to get a "molecular sieve" effect where the rate and extent of adsorption is sharply dependent upon the steric requirements of the amine. The use of Dowex-50 in 1,2-dimethoxyethane was decided upon as a result of an investigation of the degree of swelling of Dowex-50 in a number of anhydrous ethers.

As can be seen from an examination of Table I, the resin is not only swollen to a rather high degree in 1,2-dimethoxyethane, but there is also a strong variation of the degree of swelling with the extent of divinylbenzene crosslinkage.

TABLE I

SWELLING OF DRY DOWEX-50 IN THE HYDROGEN FORM

Cross linkage (% Divinylbenzene)	Solvent	Max. Swelling, % vol.	Time, hr.
4	Water	215	0.25
4	$CH_3OCH_2CH_2OCH_3$	110	0.5
4	$CH_3(OCH_2CH_2)_2OCH_3$	92	1
4	1,4-Dioxane	100	24
8	Water	115	0.25
8	$CH_3OCH_2CH_2OCH_3$	93	2
8	$CH_3(OCH_2CH_2)_2OCH_3$	80	2
8	1,4-Dioxane	75	24
12	Water	85	0.25
12	$CH_3OCH_2CH_2OCH_3$	60	2
12	$CH_3(OCH_2CH_2)_2OCH_3$	55	2
12	1,4-Dioxane	35	48

It is seen that the degree of swelling decreases with increasing crosslinkage in each case. The rate of swelling in dioxane is slow, requiring forty-eight hours for maximum swelling in the case of the 12% crosslinked resin. The degree of swelling for 1,2-dimethoxyethane and also dimethyl ether of diethylene glycol is appreciable and differs markedly for resins of different crosslinkage. Moreover the time required for attainment of maximum swelling is reasonable.

Table II summarizes the results of the batchwise extraction of some arylamines by Dowex-50 preswollen in 1,2-dimethoxyethane. The amine uptake is stated as milliequivalents of amine adsorbed per gram of resin (dry basis).

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(1) R. Kunin, G. W. Bodamer, *Ind. Eng. Chem.*, **45**, 2577 (1953).

(2) Ansul Ether-121. All glycol ethers were supplied by Ansul Chemical Co., Marinette, Wis.

TABLE II

Adsorption of Some Arylamines at 25° by Dowex-50 in 1,2-Dimethoxyethane (meq./g.)

Amine	Time, hr. 1	2	3	4	5	6	24	96	120
				4% Crosslinked Resin					
Aniline	2.1	2.3	2.6	2.7	2.9	—	3.5	3.5	3.5
N,*N*-Dimethylaniline	0.9	1.7	2.3	2.5	2.6	2.7	3.2	3.3	3.3
3,5-Dimethylaniline	1.3	1.5	1.7	2.0	2.1	2.2	3.0	3.3	3.3
2,4-Dimethylaniline	1.1	—	1.5	1.7	1.9	2.2	2.6	2.8	2.8
N-Methylaniline	1.1	1.4	1.5	1.6	—	1.7	2.6	2.7	2.7
2,5-Dimethylaniline	1.1	—	1.4	1.7	1.9	2.0	2.3	2.6	2.6
2,6-Dimethylaniline	0.8	0.9	1.1	1.7	—	—	2.2	2.5	2.6
				8% Crosslinked Resin					
N,*N*-Dimethylaniline	0.9	1.7	2.3	2.5	2.6	2.7	3.1	3.3	3.3
Aniline	0.9	0.9	1.2	1.3	1.4	—	2.4	2.7	2.8
3,5-Dimethylaniline	0.9	1.1	1.3	1.4	—	1.6	2.5	2.6	2.6
2,5-Dimethylaniline	0.8	0.8	1.0	1.1	—	—	2.0	—	2.5
2,4-Dimethylaniline	0.7	—	0.7	0.7	0.9	1.2	1.6	2.1	2.2
2,6-Dimethylaniline	0.5	0.7	0.7	0.8	0.9	—	1.4	1.8	1.8
				12% Crosslinked Resin					
Aniline	0.3	0.8	1.1	1.1	1.2	1.4	1.9	2.4	2.4
3,5-Dimethylaniline	0.5	0.7	1.2	1.3	1.4	—	1.9	2.3	2.3
N,*N*-Dimethylaniline	0.5	0.6	0.7	0.8	0.9	0.9	1.7	2.2	2.3
2,4-Dimethylaniline	0.2	0.3	0.4	0.5	0.6	—	1.0	1.5	1.5
2,5-Dimethylaniline	0.1	0.3	0.4	0.5	0.5	—	1.0	1.5	1.5
2,6-Dimethylaniline	0.2	0.3	0.5	0.5	0.6	—	0.9	1.3	1.4

It is noted that at constant temperature and concentration the rate of adsorption is a function of the resin crosslinkage and the type of methyl substituted amine. The values for the 4% crosslinked resin illustrates the behavior of the resin with the largest pores. Here the amines are adsorbed in the order aniline>3,5-dimethylaniline or *N*,*N*-dimethylaniline, >2,4-dimethylaniline > *N*-methylaniline > 2,5-dimethylaniline > 2,6-dimethylaniline. Apparently steric factors are important although the relative position of *N*,*N*-dimethylaniline may be attributed to difference in base strength. As might perhaps be expected in this case the differences in amine uptake are not well pronounced. The amines fall generally into two groups, aniline, *N*,*N*-dimethylaniline, and 3,5-dimethylaniline in the more strongly adsorbed group and the other amines of the series in a some what less strongly adsorbed group.

The 8% crosslinked resin illustrates the behavior of a resin of intermediate porosity. Here the order of adsorption is *N*,*N*-dimethylaniline > aniline or 3,5-dimethylaniline > 2,5-dimethylaniline > 2,4 dimethylaniline > 2,6-dimethylaniline. The position of *N*,*N*-dimethylaniline with respect to aniline can only be explained on the basis of differences in base strength. The other amines are adsorbed in an order consistent with their relative steric requirements.

The 12% crosslinked resin illustrates the behavior of the resin with the finest pores. The *ortho* methyl-substituted amines apparently do not penetrate the resin to any great extent and are largely adsorbed almost identically. *N*,*N*-Dimethylaniline is adsorbed somewhat less strongly than either of these. Apparently the steric requirements of the two *N*-methyl groups compensate for any enhanced basicity.

EXPERIMENTAL

The resins in the hydrogen form were washed first with the ether to be used in the swelling experiments, then with anhydrous diethyl ether, and then dried *in vacuo* at 60° for at least 72 hr. The ethers were dried over sodium hydroxide, refluxed over sodium borohydride in a nitrogen atmosphere to remove peroxides, and then distilled under nitrogen. The purified ethers were kept over calcium hydride under an atmosphere of nitrogen. All swelling determinations were made dilatometrically at 25°.

The amines used for the batchwise extraction of the arylamines from anhydrous 1,2-dimethoxyethane were of the highest purity available. These were dried over sodium hydroxide and redistilled at reduced pressure. In each case 12 meq. of amine and 1.5 g. (dry weight) of the preswollen resin (the capacity of this resin in water is 5.3 meq. per g.) were present in a volume of 85 ml. The experiments were run in pear-shaped flasks which were well sealed to prevent loss by evaporation and were fitted with mechanical stirrers. The design of the flasks was such as to keep the resin particles well dispersed throughout the solution during the experiments. The flasks were immersed in a thermostat at 25°. Two-milliliter samples of the solution were periodically withdrawn in duplicate, and the concentration of the amine determined potentiometrically as described in the following section. Several blank runs were made with resin and solvent in the absence of amine. Initially, under the experimental conditions used, the acidity due to the resin was negligible. However, this acidity increased slightly over a period of days and since at the same time the concentration of the amine had decreased, a correction had to be made for the values at 120 days. This correction in no case amounted to a titre of more than 0.1 ml. of $0.1N$ sodium hydroxide per aliquot. A correction also was made for the quantity of amine removed in the course of analysis. The extracted samples were analyzed by titration with $0.1N$ hydrochloric acid in 1:1 ethylene glycol-isopropyl alcohol solvent.[3] The end points were determined potentiometrically.

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(3) S. Palit, *Ind. Eng. Chem.*, **18**, 246 (1946).

A Dimer of Styrene: 1,2-Diphenylcyclobutane

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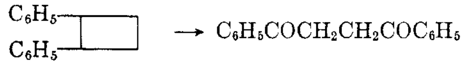
The treatment of styrene with refluxing aqueous sulfuric acid yields two dimeric hydrocarbons, the linear, unsaturated 1,3-diphenyl-1-butene, and the cyclic, saturated 1-methyl-3-phenylindan.[2,3] The free radical or thermal polymerization of stryene, on the other hand, leads to high molecular weight polymers. If the thermal reaction is conducted, however, in the presence of polymerization inhibitors such as picric acid,[4] iodine,[5] or *sym*-trinitrobenzene,[5] one again observes the formation of cyclic, saturated dimeric hydrocarbons.[6] These dimers are structurally different from 1-methyl-3-phenylindan. The present paper presents evidence that one of the dimers produced from the free radical inhibited thermal polymerization of styrene is 1,2-diphenylcyclobutane, a head-to-head dimer of styrene. Thus, the chromic oxide oxidation of the dimeric mixture yields 1,2-dibenzoylethane (diphenacyl, succinophenone).[7] This represents the first definite evidence for the preparation[4,5] and presence of 1,2-diphenylcyclobutane.



EXPERIMENTAL

Styrene. Commercial styrene was washed free of inhibitor with aqueous sodium hydroxide, dried, and distilled through a 1-meter packed column at reduced pressure.

Dimerization reaction. A solution of 0.4 g. iodine in 200 g. styrene was refluxed for 16 hr. (146°). Vacuum distillation separated the amber-colored reaction product into 100 g. of recovered monomer, 77 g. solid polymer, and 19 g. liquid oligomer. The latter was washed with aqueous sodium bisulfite and mercury to remove codistilled iodine and then distilled to yield 7 fractions (b.p. 124–160°/0.5 mm., n_D^{20} 1.5864–1.5961).[8]

Fraction 3 (n_D^{20} 1.5913) was submitted for analysis.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.1; H, 7.8; mol. wt. 208; H_2 absorption, 0.00 mole. Found: C, 92.5; H, 7.9; mol. wt. 196 (benzene); H_2 absorption, 0.03 mole.

The infrared spectra of the individual fractions differed from that of the separately prepared sulfuric acid dimer.[2] Significant differences are the presence in the latter of the methyl group absorption at 1376 cm.$^{-1}$ and the *trans*-unsaturation band at 966 cm.$^{-1}$

Oxidation of the dimer. Chromium trioxide (4 g.) was added over a period of 40 min. to a solution of dimer (1 g.) in 40 ml. glacial acetic acid at 50°. The temperature rose to 73° during the oxidation. Extraction with aqueous sodium bicarbonate gave no acidic product. After numerous washings, chromatograms on silica gel, and fractional sublimations of the residue, a small yield of colorless crystals of diphenacyl (m.p. 143–145°, lit.,[9] m.p. 144–145°) was obtained. It gives the described green color in concd. sulfuric acid solution.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.9; H, 5.5.

The diketone reacts with 2,4-dinitrophenylhydrazine to yield a brilliant crimson derivative (m.p. 219–221°). This may be the pyridazine which can arise by the condensation of the —$NHNH_2$ function with both carbonyl groups.

Anal. Calcd. for $C_{22}H_{16}N_4O_4$: N, 14.0. Found: N, 14.0.

The *bis*-2,4-dinitrophenylhydrazone of 1,2-dibenzoylethane is reported to be orange-yellow in color and to melt at 250° dec.[10]

Conclusive identification of the oxidation product as 1,2-dibenzoylethane was established by an independent synthesis of the diketone by the zinc dust–acetic acid reduction of 1,2-dibenzoylethylene.[10] The latter was prepared by the Friedel-Crafts condensation of fumaryl chloride with benzene.[11] An attempted synthesis of the diketone involving the sulfur dehydrogenation of the methyl groups of two acetophenone molecules was not successful.

The infrared spectrum (potassium bromide) of the oxidation product was identical with that of the authentic sample of 1,2-dibenzoylethane. Absorption bands are observed at 3060, 2905, 1680, 1598, 1582, 1445, 1396, 1372, 1352, 1256, 1220, 1178, 1074, 1062, 1024, 988, 946, 927, 918, 858, 775, 736, and 692 cm.$^{-1}$

Other reactions. Attempts to isolate definite products from the dimers by (a) ozonization in carbon tetrachloride solution

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(1) Present address: Texas-U. S. Chemical Co., TEXUS Research Center, Parsippany, New Jersey.

(2) M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

(3) B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954).

(4) F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).

(5) F. R. Mayo, personal communications.

(6) The author has observed a similar oligomerization of α-methyl styrene in the presence of iodine and ultraviolet radiation.

(7) M. Pailer and U. Müller, *Monatsh-Chemie*, **79**, 615 (1948) have shown that the chromic oxide oxidation of 1,2,3,4-tetraphenylcyclobutane (isolated from the photochemical dimerization of stilbene) yields 1,2-diphenyl-1,2-dibenzoylethane (bidesyl).

(8) A recent personal communication from F. R. Mayo and K. Griggs states that the application of gas chromatographic and infrared techniques reveals that a typical dimer obtained from the iodine-inhibited thermal polymerization of styrene consists of a mixture of 1,2-diphenylcyclobutane, 1-phenylnaphthalene, 1-phenyltetralin, and other components. The 1-phenyltetralin is isolated in greatest yield.

(9) W. Borsche, S. Kettner, M. Gilles, H. Kühn, and R. Manteuffel, *Ann.*, **526**, 1 (1936).

(10) C. F. H. Allen, D. M. Young, and M. R. Gilbert, *J. Org. Chem.*, **2**, 235 (1937).

(11) R. E. Lutz, C. F. H. Allen, and F. P. Pingert, *Org. Syntheses*, **Coll. Vol. III**, 248 (1955).