medium-pressure mercury lamp at ice bath temperature. The solution was agitated with a magnetic stirrer and was purged with a slow stream of nitrogen. At intervals, an aliquot of the photolysate was pipetted out and was properly diluted for spectroscopic measurements in the 400–500-nm region. The photolysis was continued until the quinone absorption at 450 nm disappeared completely.

For workup of the reaction mixture, the solvent was removed under vacuum at ~45 °C. In some experiments, crystalline compound separated on dilution with petroleum ether; the mother liquor was separated by column chromatography.

Photoaddition to *cis*-2-Butene. TCQ (2 g, 8 mmol), *cis*-2-butene (1.25 g, 22 mmol), and benzene (100 ml) were photolyzed until the quinone absorption peak disappeared (2 h). After solvent removal, the protuct (2.1 g) was chromatographed on an alumina column (grade 1, 75 g). Dioxene **4** (512 mg) was eluted first using a mixture of benzene and chloroform (1:1) and was identified by melting point and spectral data. The last fraction eluted with methanol was mainly phenol **6** (406 mg). It was crystallized from petroleum ether: mp 138–140 °C (lit.[2] mp 134 °C); ir 793, 1488, 1590, 1600, 3340 cm^{-1}; NMR τ 4.4 (1 H, OH), 2.1–2.7 (5 H, aromatic protons). The middle fractions were mixtures of **4** and **5** as indicated by the NMR. On the basis of NMR analysis of the photolysis product, the ratio of **4, 5,** and **6** was 6:2:9.

In a separate experiment, TCQ (5 g, 20 mmol), *cis*-2-butene (8 g), and benzene (250 ml) were photolyzed using filter solution containing $NaNO_2$ and sodium phthalate. The photolysis was complete in 2 h. The product was worked up and examined as above. The NMR of the product was identical with the one obtained without a filter. This was further checked by silicic acid chromatography.

Photoaddition to *trans*-2-Butene. TCQ (2 g, 8 mmol), *trans*-2-butene (3.0 g, 50 mmol), and benzene (100 ml) were photolyzed until the 450-nm peak of TCQ disappeared (1 h). Upon solvent removal, 2.5 g of yellow gum was obtained. A portion (2.1 g) was chromatographed on an alumina column (60 g) and eluted with petroleum ether. Dioxenes **4** and **5** were eluted and were identified by mixture melting points with the samples obtained from the thermal process. Finally phenol **6** was eluted using methanol–chloroform mixtures. Total recovery from the column was 60%. The ratio of **4, 5,** and **6** was 5:3:4 as estimated from the integration of the NMR spectra of the chromatographed fractions.

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Registry No.—**1,** 2435-53-2; **2,** 58866-14-1; **3,** 58894-39-6; **4,** 58866-15-2; **5,** 58866-16-3; **6,** 21464-64-2; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

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Asymmetric Adsorption of DL-Alanine Hydrochloride by Quartz

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In 1938 Karagunis and Coumoulos,[1] after reporting the resolution of an asymmetric chromium complex using a chromatography column consisting of powdered quartz, first suggested that asymmetric adsorption of racemic adsorbates on the surfaces of optically active minerals might have been the genesis of the first optically active molecules in nature. This suggestion appeared to receive abundant (if marginal) documentation[2] until 1968, when Amariglio et al.[3] were unable to repeat several critical quartz-mediated asymmetric adsorption experiments reported in the earlier literature, and thereupon concluded that all previous successful reports were uniformly erroneous. Because of these contradictions, we recently undertook[4,5] a reexamination of this question using experimental techniques not depending upon the polarimetric measurement of optical activity as a criterion for asymmetric adsorption, and using adsorbates more realistic from the viewpoint of prebiotic chemical evolution, namely, amino acids. We found[4,5] that radioactive D- and L-alanine hydrochloride enantiomers in 10^{-5} M dimethylformamide solutions were adsorbed by *d*- and *l*-quartz to the extent of 20–30% (as shown by radioactivity loss), and that *d*-quartz preferentially adsorbed D-alanine hydrochloride and *l*-quartz L-alanine hydrochloride. The extent of asymmetric (differential) adsorption was rather small, however, being only 0.96–1.75% (at the 99.9% confidence level). We have now extended these studies to DL-alanine hydrochloride, with the observation of significantly higher and more reproducible extents of asymmetric adsorption.

Several dilute solutions (ca. 10^{-5} M) of DL-alanine hydrochloride in anhydrous dimethylformamide were prepared, one set having the L enantiomer only labeled with ^3H and the other having the D enantiomer only labeled with ^{14}C. The radioactivity count for an aliquot of each stock solution was established by liquid scintillation counting, whereupon equal volumes of each solution were exposed to identical weights of carefully dried *d*- and *l*-quartz (average particle size, 96 μm) under anhydrous conditions. After equilibration, similar sized aliquots of the supernatant in each experiment were removed and recounted for radioactivity. The radioactivity counting data, percent total adsorption, and percent differential adsorption for the three experiments conducted are calculated and summarized in Table I.

It should be emphasized that each pair of *d*- and *l*-quartz experiments in Table I is mirror symmetric with respect to the quartz. That is, identical quantities of *d*- and *l*-quartz samples of identical particle size range were employed with identical quantities of each amino acid solution. Thus it follows in expt I, for example, that the amount of *unlabeled* D-alanine hydrochloride adsorbed from the racemate by the *l*-quartz must have been 17.58%, i.e., the same as the quantity of *labeled* L enantiomer adsorbed by the *d*-quartz. Thus the *total* racemate which was adsorbed by the *l*-quartz (or the *d*-quartz) in this experiment was 43.93%, the sum of no. 5 and no. 6. As seen in no. 7 of Table I, the total adsorption in the three experiments varied from 38 to 48%.

No. 8 in Table I shows the differential adsorption (A) of the D and L components of the racemic alanine hydrochloride solutions by *d*- and *l*-quartz, defined in terms of the difference in the amount of each enantiomer left in the supernatant divided by the amount of that enantiomer originally present. On this basis, the differential adsorption (A) in the three sets of experiments ranges from ca. 5.7 to 8.8% (a compared to only 1–1.8% in our earlier study[4,5]). It is even more striking if we look at the differential adsorption (B) in terms of the percent of each enantiomer adsorbed divided by the total percent of racemate adsorbed. From this viewpoint (no. 9) the differential adsorption (B) ranges from ca. 11.8 to 20.3%. From either viewpoint we see clearly that *l-quartz preferentially adsorbs L-alanine hydrochloride from a racemic mixture, whereas d-quartz favors the D enantiomer*—results which unambiguously confirm the conclusions of our earlier exper-

Table I. Experiments Involving the Adsorption of Enantiomerically Labeled DL-Alanine Hydrochloride by *d*- and *l*-Quartz

	Expt I	Expt II	Expt III
1. Labeled enantiomer in racemate	L	L	D
2. Stock solution, counts	165 331 ± 857	172 626 ± 577	82 570 ± 226
3. Supernatant over *l*-quartz, counts	121 774 ± 592	133 185 ± 525	64 976 ± 356
4. Supernatant over *d*-quartz, counts	136 273 ± 434	146 477 ± 493	60 250 ± 466
5. % adsorbed by *l*-quartz[a]	26.35 ± 0.66	22.85 ± 0.45	21.31 ± 0.54
6. % adsorbed by *d*-quartz[b]	17.58 ± 0.58	15.15 ± 0.44	27.03 ± 0.65
7. Total racemate adsorbed, %[c]	43.93 ± 0.88	38.00 ± 0.63	48.34 ± 0.85
8. Differential adsorption (*A*), %[d]	8.77 ± 0.45	7.70 ± 0.42	−5.72 ± 0.71
9. Differential adsorption (*B*), %[e]	19.96 ± 2.46	20.26 ± 2.05	−11.83 ± 2.14

[a] 100 × (no. 2–no. 3)/no. 2. [b] 100 × (no. 2–no. 4)/no. 2. [c] No. 5 + no. 6. [d] 100 × (no. 4–no. 3)/no. 2, equivalent to no. 5–no. 6. [e] 100 × no. 5/no. 7 − 100 × no. 6/no. 7.

iments[4,5] employing individual alanine hydrochloride enantiomers. We have previously discussed some of the chemical evolutionary implications of the asymmetric adsorption of amino acids by quartz.[2,5]

Experimental Section

***d*- and *l*-Quartz Powder.** Samples of dextro- and levorotatory "cultured quartz", prepared commercially by hydrothermal growth for optical and electronic applications (Sawyer Research Products, Inc., Eastlake, Ohio), were originally checked for uniform optical handedness as well as enantiomerism by direct measurement of their optical rotations with sodium D-line light. Nine large crystal samples (ca. 2 × 3 × 18 cm) of one morphological handedness had an average rotation of +21.2 ± 0.5° mm^{-1} along roughly the optical axis. Four similar crystals of enantiomeric morphological handedness showed a rotation of −26.2 ± 5.5° mm^{-1}, a less precise value since the crystal axis and optical axis were not exactly identical. The reported rotation for natural quartz along the optical axis is ±21.724° mm^{-1} for 5893 Å light.[5] Inorganic impurities in the cultured quartz employed were reportedly below the usual spectrographic detection limits (1–5 ppm) (Sawyer Research Products, Inc., quality specification brochure). Such enantiomerically homogeneous crystals were broken by impact and then ground manually using an alundum mortar and pestle.[5] Each resulting powder was subjected to a quick, initial screening with the aid of U.S. standard stainless steel sieves to give a fraction having particles between 120 and 325 mesh (44–125 μm). In a typical preparation, this fraction was divided into four smaller 15-g batches, which were then graded individually using an Allen-Bradley Model L3P sonic sifter (ATM Corp., Milwaukee, Wis.). The cut of interest between 140 and 170 mesh (88–105 μm) was collected from each batch (25–27% of the total material), combined (ca. 14.0 g), and subjected to four additional screenings using 120, 140, 170, 230, 270, and 325 mesh screens in the sonic sifter. The final product was 11.4 g of quartz powder over 99% of which had the particle size range of 88–105 μm (96-μm average; surface area ca. 0.024 m^2/g).[5] Such samples, the surface crystallinity of which has been previously established,[5] were used in the adsorption experiments below after thorough drying for 3 h at 170 °C under 0.1 Torr vacuum on the vacuum line employed in the experiments. In experiments using ^3H_2O, this drying technique has been found to be essentially 100% effective for powdered quartz.[5]

Radioactive DL-Alanine Hydrochloride Solutions. DL-Alanine (Ajinomoto, Inc., Tokyo, Japan) was dissolved in 1 N HCl. A portion of this solution was treated with a sufficient volume (ca. 20 μl) of [3-^{3}H]-L-alanine hydrochloride solution (30–50 Ci/mmol, 0.01 N HCl; no. NET-348, New England Nuclear, Boston, Mass.) to give ultimately the counts per 5-min period indicated in no. 2 of Table I. The amount of radioactive L-alanine added was insufficient to change the 50:50/D:L ratio of the racemic alanine carrier significantly. The solution was evaporated under vacuum and the residue was dried in a desiccator then was dissolved in sufficient anhydrous[5] dimethylformamide to give a stock solution 1.5 × 10^{-5} M in [^{3}H]-DL-alanine hydrochloride. A second portion of the above solution of DL-alanine in 1 N HCl was treated with sufficient [1-^{14}C]-D-alanine hydrochloride solution (5–15 mCi/mmol, 0.1 N HCl; no. NEC-446; New England Nuclear) to provide ultimately the counts during a 50-min period noted in Table I. The quantity of labeled D-alanine added was such as to make the composition of the final mixture 50.5:49.5/D:L. The solution was similarly evaporated and the residue was dissolved in sufficient anhydrous dimethylformamide to provide a 2.0 × 10^{-5} M stock solution. The above stock solutions were stored under septa until used.

Adsorption Experiments. Ten milliliters of the above 1.5 × 10^{-5} M [^{3}H]-DL-alanine hydrochloride stock solution was removed by hypodermic syringe and introduced through one septum-stoppered arm of a two-arm adapter tube into a 25-ml round-bottom flask containing 7.0 g of *l*-quartz powder prepared and dried as described above. The second arm of the adapter tube was attached through a Teflon stopcock to a vacuum line. Ten milliliters of the same stock solution was introduced into an identical flask attached to the same vacuum line and containing 7.0 g of similar *d*-quartz powder. The duplicate mixtures were stirred magnetically at room temperature for 1 h, then allowed to settle for 3 h, whereupon three 300-μl aliquots of each supernatant were removed with a hypodermic syringe. The radioactivity of each aliquot was counted during triplicate 5-min intervals using a Packard 3320 Tricarb liquid scintillation counter, as described previously,[5] providing nine 5-min counts for each supernatant. Three 300-μl aliquots of the original stock solution were similarly counted in triplicate, providing nine radioactivity control measurements on the stock solution unexposed to *d*- or *l*-quartz. The averages of such countings for duplicate experiments (columns I and II) involving [^{3}H]-DL-alanine hydrochloride are shown in no. 2, 3, and 4 of Table I, where the standard deviations range from about 0.3 to 0.5% of the total counts (av 0.38%).

A similar experiment was performed identically using 9 ml of the above 2.0 × 10^{-5} M stock solution of [^{14}C]-DL-alanine hydrochloride. Owing to the lower radioactivity level, the triplicate counting times for each aliquot in this experiment were extended to 50 min. The results are indicated in the last column of Table I. Because of the differences in alanine hydrochloride concentrations, the adsorption values in column III in Table I are not to be quantitatively compared with those in columns I and II.

Registry No.—DL-Alanine hydrochloride, 25616-13-1; quartz, 14808-60-7.

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