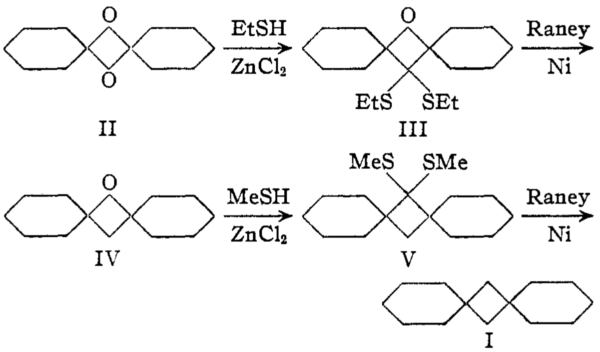
Although cyclobutan-1,3-diones (ketoketene dimers) possessing the structural features of II have been intensively studied,[3] at the time of this investigation it had not been found possible to convert them to the corresponding cyclobutanes.[4] The conversion, in the case of II, was carried out making use of a method developed for carbonyl reduction by Wolfrom and Karabinos.[5] The steps in the synthesis (outlined in the Chart) were realized without difficulty. Noteworthy is the fact that only one carbonyl function[6] in II is reactive toward mercaptans.



Experimental[7]

Dispiro(5.1.5.1)tetradecan-7,14-dione (II).[2]—Hexahydrobenzoyl chloride (140 g., 0.96 mole) and 1 liter of dry benzene were introduced into a three-necked flask equipped with stirrer, condenser and dropping funnel. An atmosphere of dry nitrogen was maintained in the reaction vessel; dry triethylamine (165 g., 1.6 moles) was slowly added with stirring. Stirring was continued and the reaction mixture was refluxed overnight. The triethylamine hydrochloride was filtered off and washed with benzene. The combined filtrates were washed with dilute hydrochloric acid and with water. Solvent was removed by distillation and the residue was recrystallized from petroleum ether–ethanol; yield 56 g. (53%) of II, m.p. 164–165° (lit.[2] m.p. 164–165°). The 2,4-dinitrophenylhydrazone of II was obtained as a difficultly soluble yellow solid, m.p. 267–268°.

14,14-Di-(ethylmercapto)-dispiro(5.1.5.1)tetradecan-7-one (III).—Freshly fused zinc chloride (1.8 g.), anhydrous sodium sulfate (1.5 g.) and II (6 g., 0.027 mole) were placed in a stoppered flask together with an excess of ethyl mercaptan (*ca.* 20 g.). The mixture was placed in the ice-chest overnight, then allowed to stand at room temperature for 24 hours and finally poured into a separatory funnel containing ice-water and ether. The ether layer was separated, washed well with 10% aqueous sodium hydroxide solution and dried. Solvent was distilled off and the residue (7.5 g., 84% yield) was recrystallized from ethanol, m.p. 57.5–58.3°.

Anal. Calcd. for $C_{18}H_{30}OS_2$: C, 66.2; H, 9.3; S, 19.6. Found: C, 66.1; H, 9.4; S, 19.2.

In a like manner II reacted with excess of methyl mercaptan in a sealed tube at room temperature. The product, the methylmercapto analog[8] of III, was recrystallized from ethanol, m.p. 110.5–110.8°, analysis for $C_{16}H_{26}OS_2$.

Dispiro(5.1.5.1)tetradecan-7-one (IV).—A mixture of 345 g. of Raney nickel, 750 ml. of ethanol and 15 g. (0.046 mole) of III was refluxed for 48 hours. The solid was separated by centrifugation and washed with hot ethanol. Solvent was distilled *in vacuo* from the combined alcoholic solutions; from the residue was obtained 7 g. (73% yield) of IV. After recrystallization from acetonitrile, IV melted at 89–90.5° and had an odor resembling that of citrus fruit.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.5; H, 10.7. Found: C, 81.3; H, 10.8.

The 2,4-dinitrophenylhydrazone of IV was crystallized from ethanol–acetonitrile, m.p. 181–182°, analysis for $C_{20}H_{26}N_4O_4$.

7,7-Di-(methylmercapto)-dispiro(5.1.5.1)tetradecane (V).—Zinc chloride (5 g.) was fused in a glass bomb tube and was allowed to solidify on the walls of the tube. While the tube was cooled in a Dry Ice–acetone-bath, there were added 5 g. of anhydrous sodium sulfate, 9 g. (0.0436 mole) of IV and 50 g. of methyl mercaptan. The tube was sealed, shaken and allowed to stand for 48 hours at room temperature. Excess mercaptan was allowed to distil off and the residue in the tube was taken up in ice-water–ether. The ether solution was washed with sodium hydroxide solution and worked up as usual, yield 6 g. (48%) of V, which, after recrystallization from ethanol (or acetonitrile), melted at 83.5–84.5°.

Anal. Calcd. for $C_{16}H_{28}S_2$: C, 67.5; H, 9.9. Found: C, 67.5; H, 10.0.

Dispiro(5.1.5.1)tetradecane (I).—Freshly prepared Raney nickel (180 g.), ethanol (500 ml.) and V (6 g., 0.021 mole) were placed in a flask and refluxed for 30 hours. The Raney nickel was centrifuged off and washed with hot ethanol. The alcoholic solutions were combined, diluted with water and extracted with petroleum ether (b.p. 60–70°). The extract was distilled through a column to remove solvent and the residue was distilled from a Claisen flask; yield 0.69 g. (17%) of I, b.p. 175–190° at 110 mm. Redistillation over sodium gave material with the following constants: b.p. 131° at 10 mm., m.p. 10°, $n^{26.8}\text{D}$ 1.4735, $d^{26.54}$ 0.872.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.4; H, 12.6. Found: C, 87.5; H, 12.6.

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[3] H. Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912; W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 108.

[4] More recently it has been shown that this type of reduction may be accomplished by the Wolff–Kishner method *via* the disemicarbazone; see H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

[5] M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944).

[6] *Cf.* T. Posner, *Ber.*, **33**, 2983 (1900); **35**, 493 (1902).

[7] Melting points are uncorrected; analyses by Dr. A. Elek, Los Angeles.

[8] II combines with trimethylene mercaptan in one to one molar ratio to give a similar derivative, m.p. 112.5–113°; see H. M. Walborsky, Ph.D. thesis, The Ohio State University, 1949.

Diffusion of Polymer Mixtures

BY GUY B. TAYLOR AND F. T. WALL

RECEIVED JULY 15, 1953

This note describes an investigation of the simultaneous diffusion of two or more substances, such as unfractionated polymers, by the experimental method of Wall, Grieger and Childers.[1]

The method consists of saturating a thin porous porcelain plate (frit) with a solution, then following its change in weight with time when it is submerged in a large volume of pure solvent while hanging by a fine wire from one arm of an analytical balance. The method employs the same principle for the actual diffusion as that of Aten and Dreve[2] except that these authors determined the quantity diffused by analytical methods.

The integrated diffusion equation in suitable form for our conditions can be written

$$(W_t - W_\infty) = \frac{16AL(d_2 - d_1)}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2\pi^2 Dt}{4L^2}\right] \tag{1}$$

where W_t is the observed weight at time t, W_∞ the weight at infinite time, A the effective area of one face of the plate, L half its effective thickness, n all integers to infinity, and D the diffusion coefficient. The term $(d_2 - d_1)$ is the difference between the density of the original solution and

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[1] F. T. Wall, P. F. Grieger and C. W. Childers, THIS JOURNAL, **74**, 3562 (1952).

[2] A. H. W. Aten and J. V. Dreve, *Trans. Faraday Soc.*, **44**, 202 (1948).

that of the outside bath, a parameter governed by the initial conditions of the experiment. By combining all of the constants, and neglecting values of n greater than zero, one obtains

$$(W_t - W_\infty) = k' \exp(-kDt) \tag{2}$$

or

$$\ln(W_t - W_\infty) = -kDt + \ln k' \tag{3}$$

where k and k' are constants.

It can be shown that except for very short time intervals, terms corresponding to values of n above zero can, indeed, be neglected; hence plots of log $(W_t - W_\infty)$ *vs.* t yield mostly straight lines with slopes equal to $-kD$ where k is a constant characteristic of the frit which can be determined by calibration with a standard. Theoretical departures from straight lines can be calculated readily, using the numerical data of Table I (an illustration of an actual case is given). The table lists values of a correction factor calculated according to the equation

$$y = \sum_{n=0}^{n=\infty} \frac{\exp(2n+1)^2 x}{(2n+1)} \tag{4}$$

for the number of n values given in the first column with $x = kDt$. The calculations were carried till the next integer ceased to increase y values in the fourth decimal place. This factor is all that is necessary to correct for non-linearity of the log plot for short times.

TABLE I

CALCULATIONS FOR THEORETICAL PLOT

n	x	y	y/e^{-x}	t	W_s	W_D	W_{obsd}
19	0.005	1.1710	1.176	1.07	283.8	333.7	...
14	.01	1.1451	1.157	2.15	282.2	326.5	...
10	.02	1.1084	1.131	4.30	279.3	316.0	319
8	.04	1.0564	1.100	8.6	273.8	301.2	305
6	.06	1.0166	1.079	12.9	268.4	289.6	292
5	.08	0.9830	1.065	17.2	263.1	280.2	282
5	.10	.9535	1.054	21.5	257.8	271.8	273
4	.12	.9267	1.045	25.7	252.7	264.1	265
4	.16	.8792	1.031	34.4	242.7	250.2	251
4	.20	.8374	1.023	43.0	233.3	238.7	238
3	.32	.7324	1.008	68.8	206.8	208.5	207
2	.50	.6078	1.002	107.5	172.9	173.3	172

The method chosen here for presenting the results involves plotting on semilog paper, with the weight in milligrams on the log scale *vs.* time in minutes. Slopes for single diffusers are calculated from the straight parts of the lines as

$$\text{slope} = \frac{2.3(\log W_1 - \log W_2)}{t_2 - t_1} = -kD$$

The calculated departure from the straight line is obtained by plotting values of $t = x/\text{slope}$ against linearly extrapolated values of $W_t - W_\infty$ multiplied by y/e^{-x} at corresponding x.

Experimental

Two jars containing 2.5 liters each of solution and solvent, respectively, were mounted on a sliding rack in a bath maintained at 20.0 ± 0.05°. Either jar could be placed in position for immersion of a plate hanging vertically from an arm of a balance above the bath. The fine platinum wire suspension was attached to a plate by passing it through a tiny hole near the plate edge. Considerable trouble was experienced by surface tension pull on the wire until the wire was platinized. This effect was particularly troublesome with aqueous systems until it was found that a trace of "Duponol" ME dry fatty alcohol sulfate in the water eliminated it entirely. The sliding rack arrangement provided for alternate quick transfer from one jar to the other so that diffusion into or out of the plate could be measured.

Although the jars were kept covered with glass plates except for a slit to accommodate the wire, organic solvents tended to change significantly in density from slight moisture pickup and accumulation of diffusate. This was corrected by occasional weighing of a glass plate kept suspended in the liquid. Whether the liquid was stirred or not between weighings seemed to make little difference in the results.

The plates which were used with unsealed edges were "Selas" porcelain of the quality designed for clarifying liquids and for bacteriological filtration. Data on their physical dimensions are given in Table II. The thicknesses were uniform within ±5%, although the plates labeled G were ground in our shops to somewhat better tolerances. It is useful, even if unnecessary, for the experimenter to know the density difference $(d_2 - d_1)$ between solution and solvent, so if V_0 is the volume of the solid substance and V the volume of the pores, the calculated change in weight for transfers from one liquid to the other at zero time is $\pm(V_0 + V)(d_2 - d_1)$ and the change attending diffusion from zero time to infinity is $\pm V(d_2 - d_1)$.

TABLE II

DATA ON THE POROUS PLATES

From Selas Company's Catalog

Code	10	G-10	G-015
Capillary radius × 10^4 cm., max.	4.4	4.4	1.4
Average	2.2	2.2	0.7
Capillaries/sq. in. (× 10^{-6})	28	28	300
Measured values			
Diameter of plates, mm.	89	89	89
Thickness, mm.	4.7	1.5	1.5
Volume of solid (V_0), ml.	11.9	3.9	4.85
Volume of pores (V), ml.	17.2	5.6	4.9
Weight change (mg.) for density difference 0.01	172	56	49
Slope for sugar	0.00465	0.0385	0.046
Slope for KCl	....	0.126	0.150

Results and Discussion

Table I gives typical data preceding the straight line portion of the curve obtained with Plate 10 for diffusion of sugar in water. Figures under W_s are calculated for a straight line with slope 0.00465 and under W_d from y/e^{-x} times W_s. The observed values, last column, were obtained from plots of weight against time on ordinary graph paper. Plots of data for diffusion in and out of the plates agreed within 2 mg. at all points, including the straight line.

Figure 1 shows results with a common plate for both sugar and potassium chloride, starting with solutions of equal density. The solutions were then mixed and the operation repeated. The observations closely check the line calculated from the averages of the other two and indicate that each substance diffuses independently. The line no longer has a straight part and cannot have one until the more rapidly diffusing material is exhausted.

Unfractionated synthetic polymers, insofar as diffusion is concerned, must be rated as mixtures and be expected to yield curved lines. This is borne out by experiment as illustrated by low molecular weight polyvinyl acetates (Fig. 2) run separately and after mixture of equal density solutions in methyl ethyl ketone. The two samples had

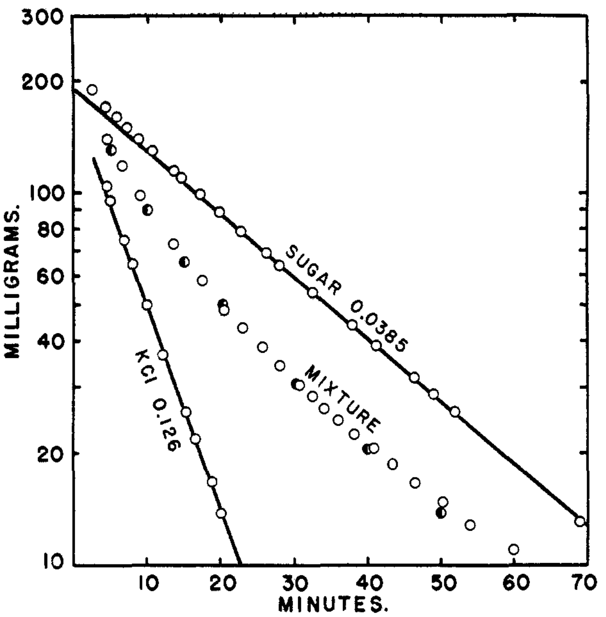

Fig. 1.—Diffusion of sugar and KCl, solutions of equal density, and equal volume mixture of the two solutions used, plate G-10: O, observed; ◐, calculated.

weight-average molecular weights of 54,000 and 8,600 as measured by light scattering. The polymer concentration was 75 g./liter.

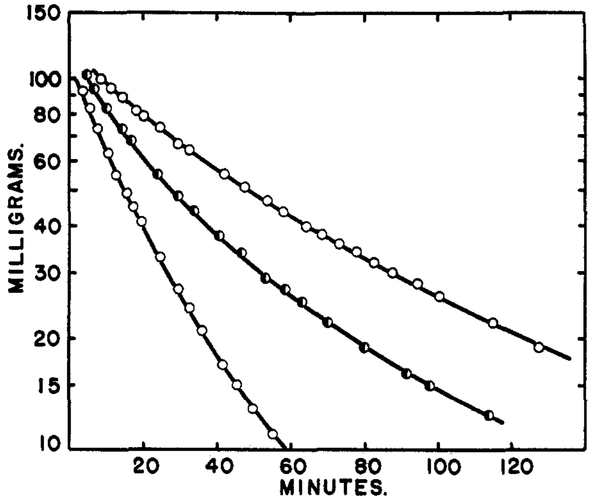

Fig. 2.—Diffusion of polyvinyl acetates (O) and mixtures of the two (◐), Plate G-015.

Measurements with really high molecular weight synthetic polymers are handicapped by the high viscosity of solutions at concentrations giving adequate density differences. The weight of solution clinging to the plate is relatively large and not easily swabbed off so as to get a clean-cut start.

It is not possible to derive any reasonable kind of average diffusion coefficient from the data for a given polymer–solvent system without making some assumption for a distribution function. It is evident that mixtures of materials having different diffusion coefficients will not give straight lines upon plotting ln $(W_t - W_\infty)$ *vs.* t. However, if the difference between the diffusion coefficients of a binary mixture is sufficiently great, the curve obtained will, after a long period of time, approach the straight line associated with the slower moving material.

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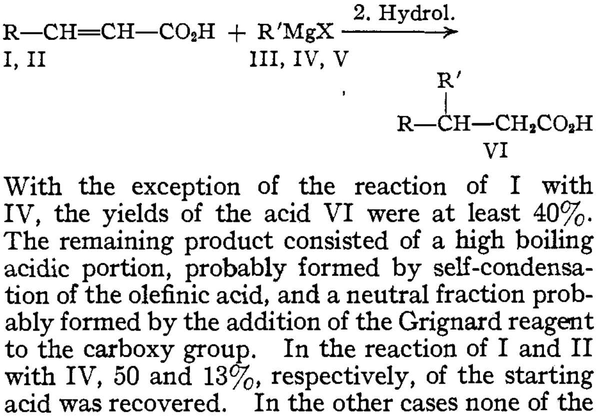
The Reaction of Grignard Reagents with α,β-Olefinic Acids

BY JOHN H. WOTIZ, JOSEPH S. MATTHEWS AND HAROLD GREENFIELD

RECEIVED AUGUST 12, 1953

Recent work in our laboratory has shown that the ethylmagnesium bromide addition product to the allenic acid, 1,2-heptadiene-3-carboxylic acid, $C_4H_9{-}\underset{|\atop CO_2H}{C}{=}C{=}CH_2$, yields upon hydrolysis 2-butyl-3-ethyl-3-butenoic acid $C_4H_9{-}\underset{|\atop CO_2H}{CH}{-}\overset{C_2H_5\atop |}{C}{=}CH_2$.[1] The reported over-all yield was 85%. The purpose of the present study was to establish whether some α,β-olefinic acids, and (or) their halomagnesium salts, also add Grignard reagents producing a new branch at the β-carbon atom. So far as we know, such reactions of Grignard reagents have not been recorded. However, the conjugate addition of Grignard reagents to α,β-unsaturated carbonyl compounds is well known. Other conjugate additions have also been reported.[2]

We have used crotonic (I), and cinnamic acid (II) and treated them with 2.5 moles of ethyl-(III), *t*-butyl-(IV), or phenylmagnesium halide (V).



$$\underset{\text{I, II}}{R{-}CH{=}CH{-}CO_2H} + \underset{\text{III, IV, V}}{R'MgX} \xrightarrow{\text{2. Hydrol.}} \underset{\text{VI}}{R{-}\overset{R'\atop |}{C}H{-}CH_2CO_2H}$$

With the exception of the reaction of I with IV, the yields of the acid VI were at least 40%. The remaining product consisted of a high boiling acidic portion, probably formed by self-condensation of the olefinic acid, and a neutral fraction probably formed by the addition of the Grignard reagent to the carboxy group. In the reaction of I and II with IV, 50 and 13%, respectively, of the starting acid was recovered. In the other cases none of the olefinic acid was recovered. Because of the ready availability of starting materials, simplicity of reaction, and relatively good yields, we consider such reactions to be of general use for the synthesis of many β branched acids.

Experimental

In the following experiments 21.5 g. (0.25 *M*) of crotonic acid (I) in 100 ml. of dry ether was added with good stirring to 0.62 mole of the Grignard in about 100 ml. of ether, at a rate to maintain refluxing. Stirring was continued for an hour at room temperature and the product was poured into a mixture of ether, ice and hydrochloric acid. Experiments where inverse hydrolysis was used gave significantly lower yields of VI. The ether layer was extracted with 10% sodium carbonate and the aqueous layer acidified with 6 *N*

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(1) J. H. Wotiz and J. S. Matthews, THIS JOURNAL, **74**, 2559 (1952).

(2) F. S. Prout, *ibid.*, **74**, 5915 (1952), and references therein.