

been employed for the preparation of 1-alkylsulfonyl-4-alkylpiperazines.<sup>12</sup> The ethanesulfonyl chloride<sup>13</sup> was prepared by the method used by Hearst and Noller<sup>14</sup> for the preparation of methanesulfonyl chloride.

The intermediate amine free base (II) was obtained from the salt by adjusting the pH of an aqueous solution from 2 to 10 with potassium hydroxide and extracting with ether. The N,N-bis-( $\beta$ -diethylaminoethyl)-amine distilled at 91–93° (1 mm.), yield 80%.

*Anal.* Calcd. for C<sub>12</sub>H<sub>29</sub>N<sub>3</sub>: N, 19.55. Found: N, 19.37.

The alkanesulfonyl chloride (0.0081 mole) in 75 ml. of absolute ether was added to a cooled, stirred solution of II (0.0163 mole) in 75 ml. of absolute ether. The reaction mixture, containing a white sirup, was stirred for two hours and permitted to stand for 15 hours. The ether was decanted and the sirup adhering to the walls of the vessel was dissolved in 5 ml. of hot 95% ethyl alcohol. Upon the addition of excess ether, the sirup crystallized. The melting point of the solid conformed to that of N,N-bis-( $\beta$ -diethylaminoethyl)-amine trihydrochloride, 185–187°.

The ether solution containing the product was evaporated to a brown oil on the steam-bath. The oil was distilled at reduced pressure to give the N,N-bis-( $\beta$ -diethylaminoethyl)-alkanesulfonamide (III) (no. 1 and 3, Table I).

**N-Substituted Alkanesulfonamides** (No. 5–10).—These compounds were prepared by treating twice the theoretical amount of the appropriate primary or secondary amine with methane or ethanesulfonyl chloride. All compounds were oils with the exception of no. 10, which was crystallized by concentrating the ether solution after removing the insoluble primary or secondary amine salt.

Yields of compounds 5 and 6 were improved by repeated extraction of the amine salt by-products with ether.

(12) R. M. Jacob, U. S. Patent 2,507,408, May 9, 1950; C. A., **44**, 7888<sup>g</sup> (1950).

(13) A. G. Kostsova, *Zhur. Obshchei Khim. (J. Gen. Chem.)*, **18**, 729 (1948); C. A., **43**, 120<sup>g</sup> (1949).

(14) R. J. Hearst and C. R. Noller, *Org. Syntheses*, **30**, 58 (1950).

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### Rates of Reaction of Diphenyldiazomethane with Aliphatic Carboxylic Acids in Ethanol<sup>1</sup>

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RECEIVED JULY 17, 1953

Roberts and co-workers have used the rates of the reaction of diphenyldiazomethane (DDM) with carboxylic acids in ethanol at 30° to obtain quantitative measurements of the relative polar effects of substituent groups.<sup>2</sup> *m*- and *p*-substituted benzoic acids in this reaction follow the Hammett equation with a rho value of +0.937.<sup>2a</sup> Linear free energy relationships between rates of the DDM reaction and corresponding ionization constants (in 50% vol. aq. ethanol) also have been found for 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids<sup>2e</sup> and for cycloalkane carboxylic acids.<sup>2d</sup> All of these cases involve rigid structures adjacent to the carboxyl group, and, except for perhaps two members of the latter series, the substitution is carried out at centers well removed from the carboxyl group.

In order to determine whether only polar effects

(1) Taken from the senior thesis of Daniel J. Smith, The Pennsylvania State College, June, 1953.

(2) (a) J. D. Roberts, E. A. McElhill and R. Armstrong, *THIS JOURNAL*, **71**, 2923 (1949); (b) J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950); (c) J. D. Roberts and E. A. McElhill, *ibid.*, **72**, 628 (1950); (d) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951); (e) J. D. Roberts and W. T. Moreland, Jr., *ibid.*, **75**, 2167 (1953).

of substituents determine rates of this reaction when less rigid and bulky groups are introduced adjacent to the carboxyl group, we have determined the rates of reaction of DDM in ethanol at 25° with a series of carboxylic acids, RCOOH. The spectrophotometric method of Roberts and co-workers has been used.<sup>2,3</sup> The second-order constants obtained are listed in Table I.

The results fit with satisfactory precision the relationship<sup>4</sup>

$$\log k/k_0 = \sigma^* \rho^* \quad (1)$$

where  $k/k_0$  is the second-order rate constant for an aliphatic acid relative to that for acetic acid;  $\sigma^*$  is the polar substituent constant for the group, R, relative to the CH<sub>3</sub> group. Values of  $\sigma^*$ , which were obtained principally from rates of alkaline and acidic hydrolysis of esters, RCOOG, have been listed previously<sup>4</sup>;  $\rho^*$  is a reaction constant measuring the relative susceptibility of the DDM reaction to polar substituents.

The value of  $\rho^*$  obtained from the present data by methods of least squares is  $+1.175 \pm 0.043$ . The median probable error of the fit of the data to equation 1 is 0.06 log unit. This is not an unsatisfactory fit in view of the uncertainties in the present data (see Experimental) and in the values of  $\sigma^*$ .<sup>4</sup> An appreciable number and variety of reaction series involving bulky groups adjacent to the reaction centers have previously been shown to fit eq. 1 with similar precision.<sup>4</sup>

TABLE I  
SECOND ORDER RATE CONSTANTS  $k_2$  FOR REACTION OF CARBOXYLIC ACIDS, RCOOH, WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ETHANOL AT 25° IN L. MOLE<sup>-1</sup> MIN.<sup>-1</sup>

Subst., R	$k_2$	Subst., R	$k_2$
CNCH <sub>2</sub>	18.5	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1.47
CICH <sub>2</sub>	12.9		
C <sub>6</sub> H <sub>5</sub> (OH)CH	6.77	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	1.09
HOCH <sub>2</sub>	3.01	C <sub>6</sub> H <sub>5</sub>	0.96
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH	2.32	CH <sub>3</sub>	.463
H	2.23	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	.442
CICH <sub>2</sub> CH <sub>2</sub>	2.24	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	.296

Figure 1 shows a plot of  $\log k_2$  vs.  $\sigma^*$ . The phenyl group provides an exception to eq. 1; the point for this group is 0.40 log unit or 500 cal./mole less than eq. 1 predicts. The deviation is in line with a specific resonance effect of the phenyl group similar to that suggested for the ionization of benzoic acid.<sup>4</sup>

Figure 1 illustrates that the present data require that steric effects remain constant whether R is a small group, such as H or CH<sub>3</sub>, or a bulky one such as (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH or *t*-C<sub>4</sub>H<sub>9</sub>.<sup>4</sup> Thus the change in steric interaction between substituent and the carboxyl group obtained when the former groups are replaced by the latter must remain constant between the reactant and the transition states.

Judging from the number and variety of substituent groups studied, it is implied that the DDM reaction can be used as a convenient method for determining polar substituent constants for

(3) (a) J. D. Roberts and W. Watanabe, *ibid.*, **72**, 4869 (1950); (b) J. D. Roberts, W. Watanabe and R. E. McMahon, *ibid.*, **73**, 760 (1951).

(4) R. W. Taft, Jr., *ibid.*, **75**, 4231 (1953).

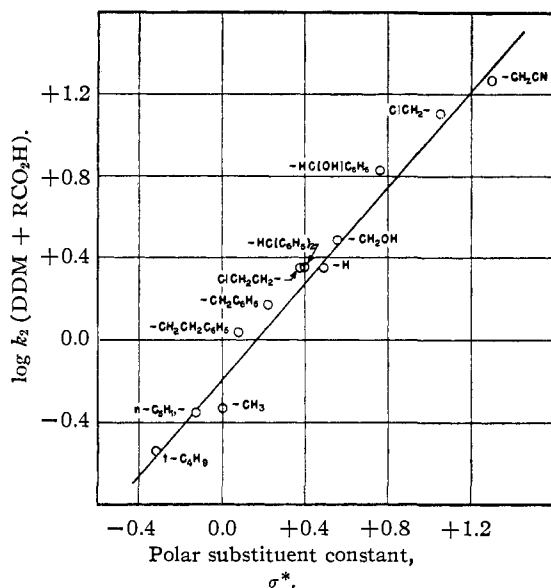


Fig. 1.—Relationship between the second-order rate constants for the reaction of diphenyldiazomethane with carboxylic acids,  $\text{RCOOH}$ , in ethanol at  $25^\circ$  and corresponding polar substituent constants,  $\sigma^*$ .

other aliphatic derivative groups. It is to be noted however that the method is not an especially good one for determining accurately small differences in polarity because of the relatively low value of  $\rho^*$ .

Figure 2 shows a plot of the logarithm of  $k_2$  for the DDM reaction with the carboxylic acids,  $\text{XCH}_2\text{COOH}$ , vs.  $\log k_2$  for the same reaction with 4-X-bicyclo[2.2.2]octane-1-carboxylic acids. A linear relationship of slope  $+4.161 \pm 0.159$  and a median deviation of 0.04 log unit is obtained. Similar demonstrations of this kind have been

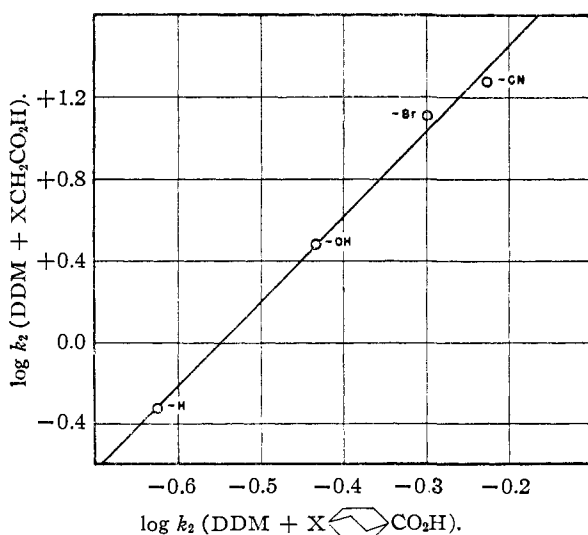


Fig. 2.—Relationship between the second-order rate constants for the reaction of diphenyldiazomethane in ethanol with carboxylic acids,  $\text{XCH}_2\text{CO}_2\text{H}$ , at  $25^\circ$  and with corresponding 4-X-bicyclo[2.2.2]octane-1-carboxylic acids at  $30^\circ$ . The point for the substituent  $-\text{CH}_2\text{Br}$  is from data for  $-\text{CH}_2\text{Cl}$ .

made for the ionization of these two series of carboxylic acids (in 50% (vol.) aq. ethanol at  $25^\circ$ )<sup>2e</sup> and for the polar effects of substituents in the alkaline hydrolysis of the ethyl esters of these two series of acids.<sup>4</sup>

These three relationships of quite satisfactory precision illustrate an important property of the electrical effects of groups on reaction rates and equilibria. In the series of bicyclooctane derivatives the X's are held essentially at a fixed distance from the carboxyl group. In the aliphatic derivatives the  $\text{XCH}_2$  groups must certainly rotate differently about the carboxyl group as one replaces H by OH, Br or CN because of the variable potential barriers to this rotation.<sup>5</sup> This rotation factor will cause both variable rotational entropies and effective distances between the reaction center and the C-X dipole. Thus if reactant states alone were involved in determining rates or equilibria, the rotation factor should be, according to either the inductive or field theories of electrical effect, a sufficient one to upset the simple type of relationship illustrated in Fig. 2.

The existence of these relationships must therefore mean that the variable rotation factor for the  $\text{XCH}_2\text{COOH}$  acids very nearly cancels between the reaction transition (or product) and the reactant states. This conclusion illustrates again how essential it is in considering problems of the present nature to take into account the fact that rates and equilibria are determined by differences between two rather than single states.<sup>6</sup>

The present and previous correlations point strongly to the fact that except for the cases in which there are variable steric or resonance interactions of substituents between reactant and transition or product states, there is a practical cancellation of the factors associated with kinetic energies of motion which makes the relative rate or equilibrium constant an essentially quantitative measure of an intrinsic electrical property of the substituent.<sup>4</sup> The very general and simple additive and proportional nature of the polar effects of groups on rates and equilibria<sup>4</sup> no doubt follows for this reason.

#### Experimental

**Rate Measurements.**—The reaction rates of diphenyldiazomethane (DDM) were measured by following the decrease in optical density at  $525 \text{ m}\mu$  of solutions of DDM and carboxylic acids with a Beckman spectrophotometer (model DU). Procedure essentially identical with that of Roberts and co-workers<sup>2,3</sup> was used. Reactions were followed for a period of one to two half-lives of the DDM. By using appreciable excess of initial acid concentrations over that of DDM, pseudo first-order kinetics were observed of the same precision (1%) obtained by the earlier workers.<sup>2,3</sup> Two to five rate determinations were made on each acid, varying the initial acid concentration. The second-order rate constants were obtained by dividing the pseudo first-order constants by the acid concentrations. In nearly every case the individual second-order constants agree within 5% of the mean. The results are summarized in Table II. Initial concentrations of DDM were estimated from initial optical densities (obtained by extrapolation) and the extinction coefficient of DDM at  $525 \text{ m}\mu$ .<sup>3b</sup> All results were obtained

(5) See, for example, W. Weltner, Jr., and K. S. Pitzer, *THIS JOURNAL*, **73**, 2606 (1951); J. Gordon and W. F. Giaque, *ibid.*, **70**, 1506 (1948); J. G. Aston, G. J. Szasz and S. Isserow, *J. Chem. Phys.*, **11**, 532 (1943).

(6) Cf. ref. 4.

at  $25.0 \pm 0.1^\circ$ , by thermostating solutions in advance and by use of a thermostated cell compartment.

TABLE II

RATE DATA FOR REACTION OF DIPHENYLDIAZOMETHANE WITH CARBOXYLIC ACIDS, RCOOH, IN ETHANOL AT  $25^\circ$

Subst., R	Concn. of acid, mole/l.	Concn. of DDM, mole/l.	$k_2$ , l. mole <sup>-1</sup> min. <sup>-1</sup>
CNCH <sub>2</sub>	0.0637	0.00333	18.0
	.0429	.00308	19.0
	.0318	.00330	18.5
ClCH <sub>2</sub>	.0570	.00310	13.1
	.0380	.00305	12.7
C <sub>6</sub> H <sub>5</sub> (OH)CH	.0328	.00279	6.86
	.0539	.00302	6.68
	.0773	.00319	6.77
HOCH <sub>2</sub>	.0410	.00332	3.01
	.0730	.00319	3.02
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH	.0459	.00319	2.22
	.0306	.00310	2.34
	.0459	.00266	2.29
H	.0525	.00224	2.41
	.0965	.00354	2.32
	.0483	.00345	2.18
ClCH <sub>2</sub> CH <sub>2</sub>	.0483	.00327	2.18
	.0870	.00306	2.30
	.0438	.00316	2.22
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	.0525	.00310	2.20
	.0559	.00554	1.43
	.0559	.00495	1.49
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	.0559	.00532	1.55
	.0461	.00236	1.49
	.0461	.00230	1.40
C <sub>6</sub> H <sub>5</sub>	.0451	.00307	1.01
	.0315	.00317	1.17
CH <sub>3</sub>	.0452	.00326	0.965
	.0928	.00290	.946
	.0618	.00385	.966
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	.0758	.00347	.468
	.0505	.00332	.461
	.1516	.00330	.460
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	.0578	.00339	.449
	.0771	.00226	.433
	.0385	.00447	.445
	.0460	.00297	.297
	.0307	.00258	.307
	.0460	.00179	.284

**Materials.**—DDM was prepared from benzophenone hydrazone by the method in "Organic Syntheses."<sup>7</sup> The method was modified in that a flask and stirrer were used in place of a pressure bottle and mechanical shaker. After the reaction mixture was filtered, an equal volume of ethanol was added to the solution of DDM in pentane, and the bulk of the material was stored under refrigeration. The pentane was boiled off of small portions of the bulk material, under reduced pressure, prior to use in the rate determinations. Ethanol was then added until the desired concentration was obtained. The preparation of DDM was done by Mr. Monis J. Manning.

The anhydrous ethanol used in the present work was obtained from commercial grade ethanol by refluxing it over magnesium turnings for several hours.

The acids used were C.P. grade Fisher Scientific or Eastman organic chemicals. Benzoic acid was recrystallized from water. Diphenyl- and phenylacetic acids were recrystallized from 50% aq. ethanol. A center cut from a fractionation of *n*-caproic acid was supplied by Mr. William A. Pavelich. Other acids were used without further purification.

(7) *Org. Syntheses*, **24**, 53 (1944).

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## Reactions of Toluic Acids with Sulfur. II. 4,4'-Bibenzylidicarboxylic Acid

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The reaction of *p*-toluic acid and sulfur to form 4,4'-stilbenedicarboxylic acid and tetra-(*p*-carboxyphenyl)-thiophene has been reported in a previous paper.<sup>1</sup> The present investigations show that the reaction of *p*-toluic acid and sulfur under a pressure of hydrogen sulfide produces, in addition, 4,4'-bibenzylidicarboxylic acid. The amounts of tetra-(*p*-carboxyphenyl)-thiophene formed are greatly reduced in the presence of hydrogen sulfide, and the yields of dimer acids (4,4'-stilbenedicarboxylic acid and 4,4'-bibenzylidicarboxylic acid) are correspondingly increased. The reduction of 4,4'-stilbenedicarboxylic acid to 4,4'-bibenzylidicarboxylic acid by hydrogen sulfide in a *p*-toluic acid solution was carried out, and additional dimer acids were formed by reaction of the *p*-toluic acid with the sulfur liberated in the reaction.

Aronstein and Van Nierop<sup>2</sup> found that the action of sulfur upon *m*- and *p*-xylenes in sealed tubes gave dimethyl stilbenes which were partially reduced to dimethylbibenzyls by the hydrogen sulfide formed. The presence of even relatively unreactive substituents had a great effect on this reaction as the reaction of toluene under the same conditions gave stilbene and tetraphenylthiophene, but no bibenzyl. The substitution of a highly reactive functional group, such as the carboxyl group, would be expected to have an even greater effect than the substitution of a methyl group into the benzene ring. The effect was found to be appreciable. In contrast to the reactions of sulfur and toluene and *m*- and *p*-xylenes, which occur to a slight extent at reflux temperatures<sup>2</sup> and which are relatively rapid at  $200^\circ$ , the reactions of sulfur and toluic acids are not detectable below about  $245^\circ$ .<sup>1</sup> Furthermore, whereas *m*- and *p*-xylenes react equally well with sulfur at  $200^\circ$ , *m*-toluic acid reacts with sulfur much more slowly than does *p*-toluic acid, and the yield of stilbenedicarboxylic acid is much lower from *m*-toluic acid than from *p*-toluic acid.

### Experimental

**Materials.**—The materials used have been previously described.<sup>1</sup>

**Reaction Conditions.**—The reactions were conducted in a stainless steel bomb of 200-cc. capacity, equipped with a thermowell, valve and bursting disk, and fitted with a glass liner, open at the top. The bomb was heated without shaking by immersion in a bath of Dow-Corning 550 fluid. The time of reaction was taken from the time the thermo-

(1) W. G. Toland, Jr., J. B. Wilkes and F. J. Brutschy, *THIS JOURNAL*, **78**, 2263 (1953).

(2) L. Aronstein and A. S. Van Nierop, *Rec. trav. chim.*, **21**, 448 (1902).