ences in the contact potentials of the components. Using reduction parameters for solutes already defined in our earlier work,[4] the X_{12} data for rubber–hydrocarbons were computed at 25° and entered as the final column of Table II.

An interesting difference is noted in comparing X_{12} in the present rubber–hydrocarbon systems with similar data reported earlier for PDMS–hydrocarbons.[4] In the present case, a systematic decrease in X_{12} (and χ^*) is noted as the number of C atoms in the solute increases. In contrast, both X_{12} and χ^* increased with increasing C atoms where PDMS was the interacting polymer. The difference is due to substantial contributions to χ from equation of state ($\tilde{v}_1$, $\tilde{v}_2$) terms in the case of natural rubber. This source of contribution was very much smaller in the PDMS case.

Synthesis of Diethynylbenzenes

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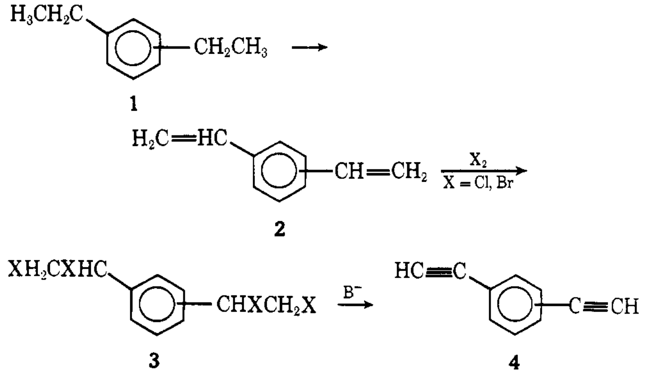
Substantial interest has recently been shown the use of diethynylbenzenes **4** in the preparation of thermally stable polymers.[1-4] The presently accepted route to these compounds is that first reported by Hay[5] (Scheme I). Although this route is in many respects acceptable, its usefulness is limited by several severe deficiencies. Among these are the difficulty of obtaining pure single isomers of diethylbenzene **1**, the tendency of the intermediate divinylbenzenes **2** to autopolymerize, low overall yields, and contamination of the product diethynylbenzenes **4** with vinylethynylbenzenes, which arise when dehalogenation rather than dehydrohalogenation of **3** occurs.

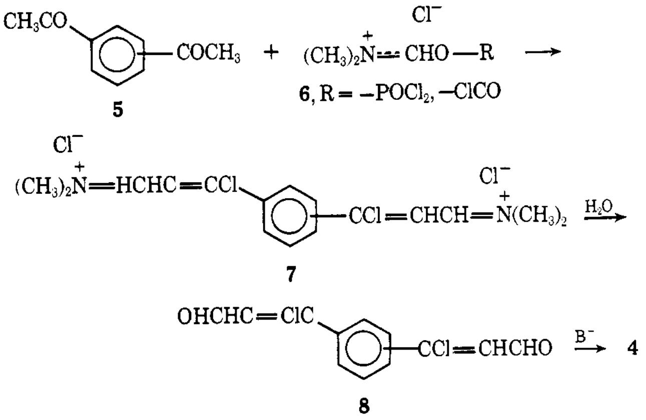
SCHEME I



Results and Discussion

We now wish to report that *m*- and *p*-diethynylbenzene (**4**) can be synthesized by dechlorocarbonylation of intermediate bis(1-chloropropen-3-al)benzenes **8**,[6] which are prepared by the reaction of the appropriate diacetylbenzene **5**[7] with a Vilsmeier complex **6**[8-14] which is prepared by the admixture of DMF with either $POCl_3$ or $COCl_2$ (Scheme II).

SCHEME II



The superiority of the present process relative to that of Hay (Scheme I) is most obvious in the case of *m*-diethynylbenzene, which can consistently be obtained in overall yields of 52–54% based on diacetylbenzene. The inherent tendency of *p*-diethynylbenzene to autopolymerize causes the yields thereof to be lower even though the yields of the intermediate β-chloroacrylaldehyde therefrom are actually superior to those obtained with the meta isomer. In addition, the remaining deficiencies of the Hay procedure are avoided herein as the product is free of vinylethynylbenzenes, and the intermediate bis(1-chloropropen-3-al)benzenes **8** are stable solids.

While either $POCl_3$ or $COCl_2$ is a suitable complexing agent for DMF, the latter is preferred in that it provides enhanced yields. Also, when $POCl_3$ is employed, the acidic reaction mixture containing the immonium salt **7** of the β-chloroacrylaldehyde **8** must be neutralized upon hydrolysis in order to liberate the free aldehyde, as the by-products of the chlorocarbonylation reaction (PO_2Cl and H_2O) combine with additional H_2O to generate H_3PO_4 and HCl, and the immonium salt **7** is stable therein. Such neutralization is not required when $COCl_2$ is employed, as the by-products therefrom are CO_2 and H_2O.

Experimental Section

1,3-Bis(1-chloropropen-3-al)benzene using $POCl_3$. Dimethylformamide (150 ml) was placed in a 1-l. stirred reactor which was cooled in an ice bath, and $POCl_3$ (115 g, 0.75 mol) was added thereto; the resulting deep red reaction mixture was stirred with continued cooling until the temperature decreased to 15°. A solution of *m*-diacetylbenzene (50 g, 0.31 mol) in DMF (75 ml) was added and the temperature of the resulting reaction mixture was maintained at 40° until the spontaneous reaction subsided (approximately 1 hr). Stirring at ambient temperature was continued for 18 hr; the reaction mixture was again cooled in an ice bath and was

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hydrolyzed with an ice–H_2O slurry (500 ml). The hydrolysate was stirred for 30 min and was then neutralized with sodium acetate (296 g), whereupon the product precipitated as a yellow solid. The crude product was isolated, washed with H_2O, and dried. The yield was 52.5 g (66.3%) of a light yellow powder, mp 114–118°. Recrystallization (2-propanol-*p*-dioxane) gave a product with mp 123.5–127°. The nmr spectrum (CH_3NO_2) was consistent with the structure of 1,3-bis(1-chloropropen-3-al)benzene (**8**): δ 6.7 (d, 2 H, -CH=, $J = 6.5$ Hz), 7.8 (m, 4 H, H_{arom}), 10.1 ppm (d, 2 H, -CHO, $J = 6.5$ Hz). The ir spectrum contained a strong band at 1660 cm^{-1} (C=O).

1,3-Bis(1-chloropropen-3-al)benzene using $COCl_2$. Dimethylformamide (100 ml) was added to a 250-ml flask fitted with a gas dispersion tube and a dewar condenser, and $COCl_2$ (17.3 g, 0.17 mol) was dispersed thereinto over a 4-hr period. The resulting complex was treated with *m*-diacetylbenzene (13.8 g, 0.085 mol) with cooling to maintain the reaction temperature at 60° and was then stirred overnight at ambient temperature. Addition of H_2O (750 ml) caused the precipitation of crude product which was isolated and washed with additional H_2O. The yield was 17.0 g (78.5%) of a light yellow powder, mp 92–103°.

1,4-Bis(1-chloropropen-3-al)benzene using $POCl_3$. The 1,4 isomer was prepared in a manner identical with that employed tor the 1,3 isomer (described above). The yield was 81% of a yellow powder, mp 145–155°.

1,4-Bis(1-chloropropen-3-al)benzene using $COCl_2$. The 1,4 isomer was prepared in a manner identical to that employed tor the 1,3-isomer (described above). The yield was 74.2% of a light yellow powder, mp 150–158°.

***m*-Diethynylbenzene.** Crude 1,3-bis(1-chloropropen-3-al)benzene (mp 114–118°, 30 g, 0.11 mol) was added to a solution of NaOH (20.0 g, 0.5 mol) in H_2O (250 ml) and *p*-dioxane (400 ml) at 75°. The resulting mixture was stirred at 75° for 45 min, cooled to room temperature, neutralized with 10% aqueous HCl (125 ml), and saturated with NaCl. Extraction with ether gave an organic solution which upon distillation gave a product, bp 46–48° (1.0 mm), which was shown to be *m*-diethynylbenzene by comparison with authentic material (prepared by the method of Hay, Scheme I). The yield was 9.7 g (69.5%).

***p*-Diethynylbenzene.** *p*-Diethynylbenzene was prepared in a manner analogous to that described above for *m*-diethynylbenzene with the exception that the product was isolated by sublimation. Owing to extensive polymerization during the isolation process, yields were limited to 20%. Analysis was by comparison with authentic *p*-diethynylbenzene (prepared by the method of Hay, Scheme I).

Communications to the Editor

On the Kinetics of Cooperative Processes. Closure Approximations

In recent years we have formulated in analytical hierarchic form the master equation for the kinetics of cooperative processes for a two-state model with nearest-neighbor interactions on a linear lattice.[1,2] In the equilibrium limit of the theory, well-known results previously derived from a partition function are obtained for infinite as well as finite chains by means of the principle of detailed balancing.[2,3]

A basic difficulty, already encountered by Glauber,[4] whose starting point is a master equation for the state probability of the whole system, arises in the nonequilibrium case. The variables in our theory are the time-dependent probabilities $n(X_j)$ for a specific sequence of states X_j with length $j > 1$. Under reversible conditions and in contrast to the irreversible case, no rate equations for sequences of arbitrary length can be formulated by inspection. A general procedure for obtaining the successive rate equations for the $n(X_j)$'s was developed[1] and applied to sequences up to length six,[2] but it becomes rapidly impracticable to carry out such a program as j increases, since the rate equations do not "close." That is, they are of the type

$$\mathrm{d}n(X_j)/\mathrm{d}t = \sum_{i=1}^{j+1} A_i n(Y_i) \qquad \text{not all } A_{j+1} = 0 \qquad (1)$$

where the A_i's are linear combinations of the rate constants. Thus, when $j = 6$, the limit to which the equations for the infinite chain have been formulated explicitly,[2] runs of length seven must be introduced, and so forth. In finite chains of sufficiently short length, this presents no difficulties, and the appropriate equations have been developed[5] for chains of up to length seven.

As in other many-body problems, a closure of the hierarchy of equations is one way out to be explored. That is, we *assume*[1,2]

$$n(Y_i; Z_j; U) = n(Y_i; Z_j)n(Z_j; U)/n(Z_j) \qquad i = 0, 1, \ldots \qquad (2)$$

Here Y_i and Z_j represent specified sequences of the two states of lengths i and j, respectively, and U is a singlet. Physically, this implies the hope that with increasing length, the behavior of short sequences should become increasingly less dependent on that of long runs.

We have tested numerical solutions of the now nonlinear differential equations by varying the magnitudes of the rate parameters over a wide range and assuming closure at levels $j = 3$ and 4, respectively.[2] Singlet, doublet, and triplet probabilities as well as number- and weight-average sequence lengths are examined as the system passes from one toward a second equilibrium state. No significant differences between the two sets of approximations are observed. This, of course, may be indicative of a good approximation or of results which vary but slowly with the level at which closure is imposed. This question remains to be investigated.

Recently, in dealing with the same subject, and based on the identical model, certain results have been put forward.[6] These involve some misconceptions about the nature of our solution and a rederivation of several of our relationships. Most basically, however, this paper includes the hypothesis that the closure approximation, eq 2, is rigorous at the triplet ($j = 2$) level. This assertion, apparently, is deduced from the fact that interactions between adjacent sites only are assumed in the elementary reaction processes. At equilibrium, of course, exact closure obtains already at the doublet ($j = 1$)

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