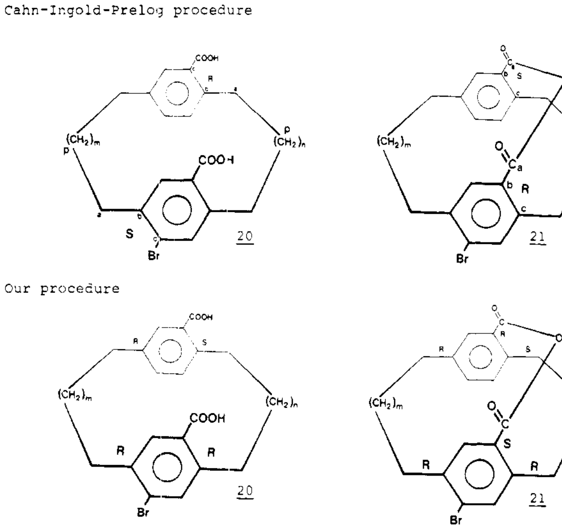
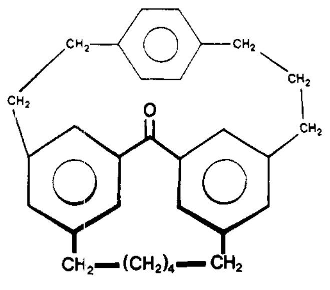


inversion of the label is the result of the Cahn–Ingold–Prelog procedure and of two chiral axes which are viewed as chiral planes (**21**). Indeed, according to our definition the acid **20** has two chiral planes in each phenyl ring. In the anhydride **21** these same chiral planes can be found and they have the same absolute configuration label as in the acid **20**. The carboxylate groups which are free to rotate in the acid can not rotate in the anhydride, which results in two new chiral elements, which are chiral axes (see definition of Hirschmann and Hanson) and not chiral planes. As can be seen the axes have the inverse label with respect to the same chiral elements viewed as chiral planes in the original paper.

Also structure **22** can be found in the paper of Cahn, Ingold, and Prelog. The phenyl–CO bonds can not rotate and this gives rise to two chiral axes and not to chiral planes as mentioned by the authors. Application of the procedure for specifying chiral axes results in the opposite absolute configuration labels with respect to the labels assigned by the authors according to their procedure for chiral planes.



22

Concluding Remarks

We hope to have brought some convincing arguments for the necessity of a new definition for the plane of stereoisomerism and a new procedure for the specification of planar chirality. Although we are aware of the practical problems created by the eventual inversion of the absolute configuration labels assigned to chiral planes, we think that something has to be done about this. In the near future the confusion about the ambiguity of the now generally used rules will be greater than the transient confusion caused by the use of new rules. We all overcame the transition from D and L into *R* and *S*. The present problem is a minor one, compared to that. By the use of the new procedure most structures with planar chirality will get two configuration labels, whereas they get only one label by the Cahn-Ingold-Prelog procedure. Therefore, there usually will be an outward sign to indicate which nomenclature is followed.

We already mentioned the great resemblance between the definitions of the axis and the plane of stereoisomerism. The distinction between both elements of stereoisomerism is more or less artificial. In both cases we are concerned with an assembly of differentiated atoms around a linear core T_1–T_2. Therefore it would be better to join both types of elements of stereoisomerism in one group of "lines of stereoisomerism". Since our new procedure for the specification of planar chirality is almost the same as the Cahn-Ingold-Prelog procedure for the specification of axial chirality, this junction does not cause any problems. We would gladly cooperate with any efforts in this direction.

Acknowledgment. We are very indebted to Professor Dr. Hans Hirschmann for the constructive comments he made during the preparation of our manuscript and for his comprehension of our viewpoints. Without the patient and profound discussions with him we should not have come to the present version of our paper.

Heterogeneous Ethylation of Phenylacetonitrile

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Data are reported relevant to the ethylation of phenylacetonitrile (PAN) in aqueous–organic medium under the standard conditions adopted for "phase-transfer reactions" in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB). The kinetic profile of the reaction has been investigated as a function of variables such as stirring rate, temperature, and concentration of the components of the reaction mixture. The experimental observations are consistent with an interfacial-type process where the quaternary ammonium salt functions as a transfer agent which resides primarily in the organic phase.

In the course of our previous studies[1-4] on the activity of macromolecular amines and ammonium salts as catalysts in reactions, such as alkylation of phenylacetonitrile (PAN) and dichlorocarbenation of styrene and benz-

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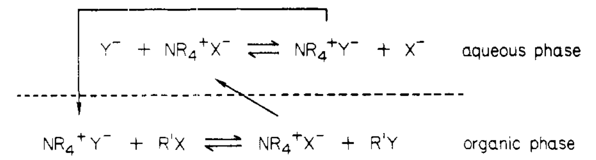
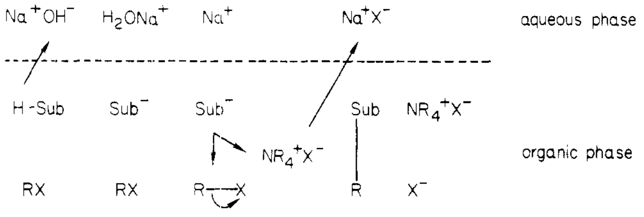
Scheme I



Scheme II



aldehyde, which are carried out under phase-transfer conditions, we have obtained data which deserve some comment. The low but definite optical rotation of the reaction products observed when optically active functional polymers were used as catalysts clearly shows the effective participation of the macromolecules in the reaction while the gradually decreased catalytic activity of the recycled polymers is to be attributed to a base-catalyzed decomposition of the ammonium salts, analogous to what has been observed in the case of corresponding low molecular weight model compounds.[5,6]

The most striking finding was the clear dependence of the reaction rate upon stirring rate, which seems to be in contrast with the suggested mechanism for "phase-transfer" reactions.[7-15] According to this mechanism (Scheme I) the ammonium salt ($NR_4^+X^-$) acts as a carrier of hydroxide ion from the aqueous to the organic phase while halogen anions are concurrently transferred from the organic into the aqueous phase.

An alternative mechanism, which was reported[5,16-18] while this work was in progress, suggests that in the case of reactions carried out in the presence of concentrated aqueous NaOH an interfacial mechanism is operative. Accordingly, as is generally accepted, deprotonation of PAN occurs only at the aqueous/organic interface while the ammonium salt acts as a carrier of the organic anion from the interface to the bulk organic phase (Scheme II).

In order to compare the activities of different catalysts in the alkylation of PAN, one finds it necessary to have a better understanding of the dependence of the reaction rate on the various reaction parameters. However, since the reaction already appears to be very complicated due to the heterogeneity of the reaction mixture, a low molecular weight catalyst was used in order to eliminate possible polymer effects. Thus the ethylation of PAN with bromoethane (EtBr) was carried out in the presence of 50% aqueous NaOH by using tetrabutylammonium bromide (TBAB) as catalyst, and the dependence of the reaction rate on the concentration, stirring rate, and temperature was studied.

Table I. Ethylation of PAN at Different Stirring Rates[a]

run	stirring rate, rpm	reaction rate, mol L^{-1} s^{-1}
P1	35	1.2×10^{-5}
P2	110	4.0×10^{-5}
P3	200	6.2×10^{-4}
P4	265	1.9×10^{-3}
P5	530	5.6×10^{-3}
P6	990	1.3×10^{-2}
P7	1950	1.9×10^{-2}
P8[b]	1950	5.3×10^{-6}
R1	1150	3.1×10^{-2}
R2	1550	6.2×10^{-2}
R3	1850	7.0×10^{-2}
R4[c]	1500	1.8×10^{-1}
R5[c]	1850	2.5×10^{-1}

[a] Reaction conditions: 40 mL of a mixture of PAN (4.85 M), EtBr (5.79 M), and TBAB (11.5×10^{-3} M) and 80 mL of 50% aqueous NaOH at 55 °C. [b] Reaction carried out in the absence of TBAB. [c] 5 mL of organic phase and 170 mL of 50% aqueous NaOH.

Table II. Ethylation of PAN at Different Temperatures[a]

run	T, °C	reaction rate, mol L^{-1} s^{-1}
P9	25	1.2×10^{-3}
P10	35	6.2×10^{-3}
P11	45	9.3×10^{-3}
P12	55	2.8×10^{-2}

[a] Reaction conditions: 40 mL of a mixture of PAN (4.85 M), EtBr (5.79 M), and TBAB (11.5×10^{-3} M) and 80 mL of 50% aqueous NaOH; stirring rate 1150 rpm.

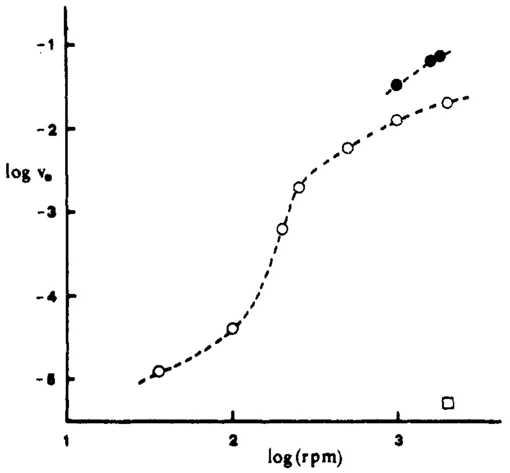


Figure 1. Dependence of the initial rate of disappearance of PAN (v_0) on the stirring rate (revolutions per minute): ○, runs P1–P7 carried out in a round-bottom flask; □, run P8 carried out in the absence of TBAB; ●, runs R1–R3 carried out in a high-mixing-efficiency reactor.

Results and Discussion

Influence of Stirring Rate. The ethylation of PAN was carried out at 55 °C by using a stirring range of 35–1950 rpm (runs P1–P8, Table I). Contrary to the reported observations[18] the rate of disappearance of PAN

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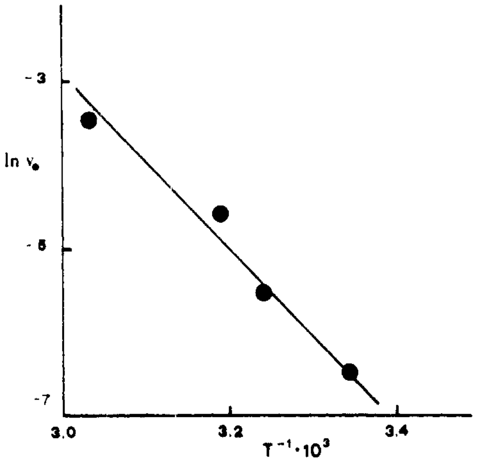

Figure 2. Dependence of the initial rate of disappearance of PAN (v_0) on temperature (runs P9–P12).

Table III. Ethylation of PAN at Different Catalyst Concentrations[a]

run	[TBAB], mmol L^{-1}	reaction rate, mol L^{-1} s^{-1}
P13	12.5	3.9×10^{-3}
P14	25	6.7×10^{-3}
P15	50	1.1×10^{-2}
P16	100	1.5×10^{-2}
P17	200	2.4×10^{-2}
P18	400	3.4×10^{-2}

[a] Reaction conditions: 40 mL of a mixture of PAN (4.85 M), EtBr (5.79 M), and TBAB at the given concentration and 80 mL of 50% aqueous NaOH; temperature 40 °C; stirring rate 400 rpm.

steadily increased with stirring rate from 1.2×10^{-5} to 1.9×10^{-2} mol L^{-1} s^{-1} (Figure 1), and still larger values (up to 2.5×10^{-1} mol L^{-1} s^{-1}) were observed when the reaction was carried out in a high-mixing-efficiency reactor (runs R1–R5). Quite interestingly, the largest increase (about 20-fold) was observed when the stirring rate was increased from 110 rpm (run P2), where the organic and aqueous phases still are two separate layers, to 200 rpm (run P3), where the two phases are intimately mixed. It is worth mentioning that in a generally accepted phase-transfer process the reaction rate becomes independent of the stirring rate above 250 rpm.[9]

In the absence of catalyst (run P8) the reaction rate does not decrease with increasing conversion. On the contrary, it increases with reaction time, probably due to the partial hydrolysis of PAN and the subsequent in situ formation of a small amount of tetraethylammonium bromide which can act as a catalyst.[19]

Temperature Effect. Four runs were carried out at 25, 35, 45, and 55 °C, respectively (runs P9–P12, Table II), with a stirring rate of 1150 rpm. From the Arrhenius plot (Figure 2) of the reaction rate vs. the temperature it is possible to evalutate an activation energy of about 20 kcal/mol.

Concentration Effects. (a) Catalyst. The dependence of reaction rate on catalyst concentration was investigated at 40 °C by using TBAB concentrations within the range 0.0125–0.400 mol L^{-1} (runs P13–P18, Table III). A bilogarithmic plot of reaction rate vs. catalyst concentration fits a straight line with slope of 0.6 (Figure 3). Such a dependence of reaction rate on TBAB concentration implies that PAN deprotonation and subsequent transfer of the organic anion from the interface to the bulk organic phase are not fast as those for the alkylation reaction. In fact, if the only rate-limiting step is the nucleophilic substitution, as in the case of S_N2 reactions, the experimental reaction rate should depend linearly on catalyst concentration.[10]

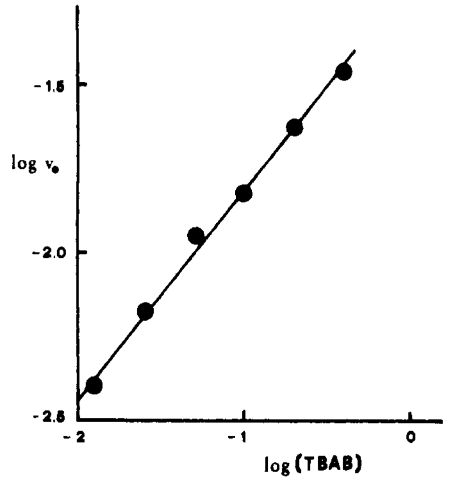

Figure 3. Dependence of the initial rate of disappearance of PAN (v_0) on TBAB concentration (runs P13–P18).

Table IV. Ethylation of PAN at Different PAN and EtBr Concentrations[a]

run	[PAN], mol L^{-1}	[EtBr], mol L^{-1}	reaction rate, mol L^{-1} s^{-1}
P19	6.6	3.3	6.5×10^{-3}
P20	5.3	5.3	8.4×10^{-3}
P21	3.8	7.6	8.7×10^{-3}

[a] Reaction conditions: 40 mL of a mixture of PAN and EtBr at the given concentrations and TBAB (17.5×10^{-3} M) and 80 mL of 50% aqueous NaOH; temperature 40 °C; stirring rate 400 rpm.

Table V. Ethylation of PAN at Different NaOH Concentrations[a]

run	[NaOH], mol L^{-1}	reaction rate, mol L^{-1} s^{-1}
P22	19	3.8×10^{-3}
P23	15	1.3×10^{-3}
P24	13	5.3×10^{-4}
P25	11	2.2×10^{-4}

[a] Reactions conditions: 40 mL of a mixture of PAN (1.16 M), EtBr (11.6 M), and TBAB (6.8×10^{-3} M) and 80 mL of 50% aqueous NaOH; temperature 40 °C; stirring rate 400 rpm.

(b) Phenylacetonitrile and Bromoethane. Three runs were carried out at molar ratios of PAN/EtBr of 2.0, 1.0, and 0.5, respectively (runs P19–P21, Table IV). Since the reactions were carried out in the absence of any organic solvent, a wider range of molar ratios was not investigated in order not to greatly modify other variables such as density and dielectric costant. The reaction rate seems, at last within this limited number of experiments, to be linearly dependent upon both PAN and EtBr concentrations.

(c) Hydroxide. Four runs were carried out in the presence of aqueous solutions of NaOH having concentrations between 19 and 11 mol L^{-1} (runs P22–P25, Table V), and, correspondingly, the reaction rate decreased from 3.8×10^{-3} to 2.2×10^{-4} mol L^{-1} s^{-1}. A bilogarithmic plot of the reaction rate vs. NaOH concentration fits a straight line having a slope of 5.3 (Figure 4). It must be noted, however, that the reaction rate depends on other factors (such as the density of the solution, the salt effect, the

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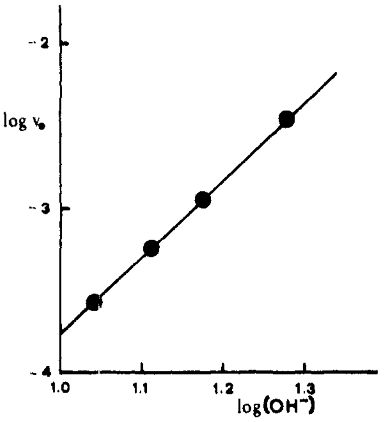

Figure 4. Dependence of the initial rate of disappearance of PAN (v_0) on NaOH concentration (runs P22–P25).

Table VI. **Ethylation of PAN at Different NaBr and NaOH Molar Ratios**[a]

run	[NaBr], mol L^{-1}	[NaOH], mol L^{-1}	reaction rate, mol L^{-1} s^{-1}
P26	0	19.0	2.7×10^{-2}
P27	0.45	18.6	1.0×10^{-2}
P28	0.9	18.1	5.6×10^{-3}
P29	1.8	17.2	2.8×10^{-3}
P30	0	18.0	2.0×10^{-2}
P31	0.6	18.0	6.7×10^{-3}
P32	1.1	18.0	4.8×10^{-3}

[a] Reaction conditions: 40 mL of a mixture of PAN (4.85 M), EtBr (5.79 M), and TBAB (0.09 M) and 80 mL of an aqueous solution of NaOH and NaBr at the given concentrations; temperature 40 °C; stirring rate 400 rpm.

activity coefficient, and the basicity of hydroxide) which, in turn, are all dependent on NaOH concentration. According to the phase-transfer mechanism, by increasing the NaOH concentration the quaternary ammonium hydroxide in the organic layer is increased both by the salting out effect and mass law. On this basis, the expected enhancement of the reaction rate should be of only a factor[20] of 1.1 for the former effect and 1.7 for the latter, whereas an increase of 1 order of magnitude higher than the expected one is observed. This difference might be tentatively ascribed to a dramatic increase of the basicity of hydroxide ions with the increasing NaOH concentration.[15] The experimental findings, therefore, better match an interfacial mechanism than a phase-transfer one.

(d) Bromide. In order to investigate the dependence of the reaction rate on the concentration of added anions, we carried out two sets of experiments in the presence of sodium bromide (Table VI; the bromide ion was chosen because it is already present as a byproduct). In the first set of experiments (runs P26–P29) NaBr and NaOH concentrations were varied between 0 and 1.8 mol L^{-1} and 19 and 17.2 mol L^{-1}, respectively, in order to keep the total salt concentration constant. Since the observed decrease, with increasing bromide concentration, of the reaction rate could also be attributed to the corresponding decrease in hydroxide concentration, a second set of experiments (runs P30–P32) was performed by varying only the bromide concentration between 0 and 1.1 mol L^{-1} and keeping the NaOH concentration constant (18 mol L^{-1}). In these cases, the reaction rate decreased again with increasing NaBr concentration as expected but to a lesser extent than in the first set due to the increasing total salt concentration.

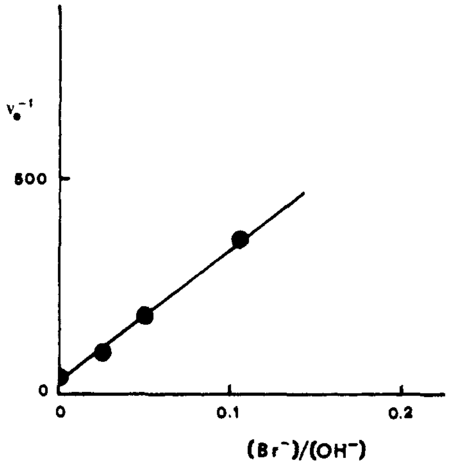

Figure 5. Dependence of the initial rate of disappearance of PAN (v_0) on the molar ratio of Br^-/OH^- (runs P26–P29).

A plot of the reciprocal of the reaction rate vs. the molar ratio of Br^-/OH^- fits a straight line (Figure 5).

According to the phase-transfer mechanism,[7–15] the reaction rate should depend on the effective concentration of the organic hydroxide as in eq 1 and 2, where n accounts

$$v_0 = k[OH^-]/([OH^-] + n[Br^-]) \qquad (1)$$

$$v_0^{-1} = k^{-1}(1 + n[Br^-]/[OH^-]) \qquad (2)$$

for the different lipophilicity of the two anions. On the other hand, on the basis of an interfacial mechanism the reaction rate should be independent of the bromide ion concentration unless a larger molar ratio of Br^-/OH^- is present at the interface than in the bulk aqueous solution (due to specific interactions of the more lipophilic anion with the organic phase) and/or there is competition between bromide and $C_6H_5\bar{C}HCN$ anions to enter the organic layer as ammonium salts.

From the values of the slope and the intercept of the plot of Figure 5 it is possible to calculate a value for n of about 100, that is, 2 orders of magnitude lower than the expected value for a phase-transfer process,[5] thus supporting further the implication of an interfacial mechanism.

Conclusions

The large dependence of reaction rate on stirring in the ethylation of PAN in a two-phase system is attributed to the operation of an interfacial mechanism in this reaction (Scheme II). As it has been shown previously, a mechanism which involves transfer of quaternary salt ion pairs between phases is independent of the stirring rate above 250 rpm.[9]

In accordance with this interfacial feature of PAN ethylation are the facts that: (a) none of the reactions studied follows pseudo-first- or second-order kinetics, (b) the reaction rate depends on catalyst concentration with a fractionary order, (c) the superlinear dependence of the reaction rate on NaOH concentration is far beyond the expected trend for classical phase-transfer-controlled reactions, and (d) the poisoning effect of the bromide ion on the catalyst activity (reflecting the dependence of the reaction rate on hydroxide ion and total salt concentration) has a value which is a factor (n = 100) of 2 orders of magnitude lower than the expected value for a true phase-transfer process. The peculiar reaction kinetics observed in the absence of a catalyst can be ascribed to the presence of small amounts of quaternary ammonium salts which are formed from PAN hydrolysis followed by in situ alkylation.

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[20] The determined content of TBAB (0.1 M) in the organic layer varies from 89% to about 100% when the hydroxide concentration goes from 11 to 19 mol/L.

As a final remark, one can state that even though the reported data do not allow one to draw a complete kinetic formulation of the reaction mechanism and further experimental work is needed these data do unambiguously demonstrate that ethylation of PAN in the presence of concentrated aqueous NaOH occurs via an interfacial mechanism.

Experimental Section

All starting materials and final products were characterized by nuclear magnetic resonance spectra recorded on a Varian T-60 NMR spectrometer using Me_4Si as internal standard.

Gas chromatographic analyses were performed on a Perkin-Elmer F30 gas chromatograph equipped with a 6 ft × $^{1}/_{8}$ in., 2% silicon gum rubber SE-30 on high-performance Chromosorb W (AW-DMCS, 80–100 mesh) column.

Reagents. Commercial grade phenylacetonitrile (PAN) and bromoethane (EtBr) were purified by distillation. Tetra-*n*-butylammonium bromide (TBAB) was prepared as reported in the literature.[21]

Alkylation Reactions. The reactions were carried out in a 250-mL, three-necked flask equipped with a condenser, thermometer, and mechanical stirrer. To a mixture of PAN, EtBr, and TBAB at a given temperature was added a solution of aqueous NaOH, preheated at the same temperature, with stirring. Stirring rates were adjusted within 1% by a Rotor revolution counter. The reaction temperature was kept constant within ±1 °C by a thermostated oil bath. Small samples of the reaction mixture were withdrawn by a syringe at intervals, quenched with dilute HCl, and extracted with diethyl ether, and the extracts were tested by GLC. Runs R1–R5 were carried out with the same general procedure but by using a reactor and a stirrer provided with additional baffles. The details of the individual experiments are given under the corresponding tables.

The initial rate of disappearance of PAN (v_0) was evaluated as the tangent to the origin of the kinetic curve.

Registry No. Phenylacetonitrile, 140-29-4; ethyl bromide, 74-96-4.

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Strained Aromatic Systems. Synthesis of Cyclopropabenzocyclobutenes, Cyclopropanaphthocyclobutenes, and Related Compounds

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The diene **9**, prepared in four steps from diethyl cyclohex-4-ene-1,2-dicarboxylate, was converted into cyclopropa[4,5]benzocyclobutene (**3**) by photoirradiation to the cyclobutene **20** followed by treatment with KO-*t*-Bu and into cyclopropa[*e*]cyclobuta[*b*]naphthalene (**45**) by Diels–Alder addition to diethyl cyclobutene-1,2-dicarboxylate, oxidation, and treatment with KO-*t*-Bu. Attempts to convert **9** into cyclopropa[*b*]anthracene were unsuccessful. The corresponding diene **15** could not be converted into cyclopropa[3,4]cyclobutabenzene (**4**), but this compound was prepared by treatment of **27**, obtained from chlorocarbene addition to bicyclo[4.2.0]octa-2,4-diene, with KO-*t*-Bu. Unsuccessful attempts to prepare substituted derivatives of **3**, **4**, and cyclopropa[*b*]anthracene as well as cyclopropa[*d*]cyclobuta[*b*]naphthalene and dicyclopropa[*b*,*d*]naphthalene are described. The chemical and physical properties of **3**, **4**, and **45** and the chemistry of the dienes **9**, **15**, and **36** are outlined, and some conclusions are drawn regarding the scope of the Billups reaction.

The extent to which the benzene ring can be distorted from its planar, hexagonal configuration before it loses its aromatic character has long interested both theoretical and experimental chemists. It is known that the out-of-plane force constants are smaller than the in-plane ones,[1] and this has been exploited in the formation of bent benzene rings, as in the paracyclophanes,[2] and in twisted benzene rings, as in layered systems.[3] Although bent and battered,[4] nevertheless the benzene rings have largely maintained the physical characteristics of the unperturbed system. Since in-plane distortions of benzene are more strongly resisted, the enforcement of changes in the in-plane geometry of benzene might be expected to more readily affect the aromatic character of the system. Such a disruption might be brought about by the introduction of large groups at adjacent positions on the ring, causing a preferred bond elongation and bond angle distortion, although the relief by an out-of-plane arrangement of the two groups can moderate such effects.[5] Alternatively, the fusion of small rings to the benzene nucleus should cause changes to both bond angles and lengths, and these would not be alleviated by the molecule becoming nonplanar. The synthesis of benzene annelated by small rings began with the preparation of biphenylene by Lothrop in 1941.[6] However, the first major impetus to work in this area was provided by Cava and his co-workers, who succeeded in preparing benzocyclobutene,[7] *sym*-dicyclobutabenzene,[8] and the two isomeric naphthocyclobutenes[9] in the late 1950's and early 1960's. The properties of these compounds showed that the benzene rings were insufficiently perturbed for their aromatic character to be disrupted. Other four-membered-ring compounds were subsequently prepared, but the next major event was the preparation of the first benzocyclopropene derivative by Anet and Anet[10] in 1964,

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