$\lambda_{\max}^{96\%\ \mathrm{EtOH}}$ 240 mμ (ϵ 13,000) and 260 mμ (ϵ 10,000) (sh), shifted to 271 mμ (ϵ 16,300) by alkali; $\nu_{\max}^{\mathrm{Nujol}}$ 3500, 3210 (NH), 1700 (sh), 1650, 1620, 1580, 1405, 1298, 1180, 803, 769, 741, and 682 cm.$^{-1}$; n.m.r. signals (60 Mc., in DMSO) at τ 2.6 (multiplet, weight 8) containing doublets at τ 2.83 (separation 9.3 c.p.s., weight ~1) and 3.90 (separation 9.2 c.p.s., weight 1).

Anal. Calcd. for $C_9H_9NOS_2$: C, 51.15; H, 4.29; N, 6.63. Found: C, 50.88; H, 4.32; N, 6.52.

If the crude product was recrystallized from aqueous ethanol, only diphenyl disulfide, m.p. 61–62°, was isolated, identified by comparison with an authentic specimen.

C. **Sodium *t*-Butyl Mercaptide.**—The reaction of *t*-butyl mercaptan with 3-isothiazolone was extremely slow in the absence of alkali. With a molar equivalent of alkali present, as in the case of sodium thiophenolate, *cis*-**3-*t*-butyldithioacrylamide** was obtained and crystallized from dry ether, on addition of petroleum ether, as colorless plates: m.p. 146–147°; $\nu_{\max}^{\mathrm{Nujol}}$ 3500, 3220, 1660, 1645, 1565, 1408, 1356, 1295, 1182, 804, 763, and 687 cm.$^{-1}$; n.m.r. signals (DMSO) at τ 2.53, 2.91 (broad, N*H*), 3.05 (doublet, separation 10 c.p.s.), 4.01 (doublet, separation 10 c.p.s.), and 8.70 (singlet).

Anal. Calcd. for $C_7H_{13}NOS_2$: C 43.94; H, 6.84; N, 7.32. Found: C, 43.81; H, 6.72; N, 7.42.

D. **Sulfide.**—To 3-isothiazolone (0.250 g., 0.0025 mole) in 1 *M* HCl (5 ml., 0.005 mole) was added sodium sulfide (0.60 g., 0.0025 mole) in 2 ml. of water. There was an immediate precipitate of sulfur (0.06 g., 75% based on sulfide). Extraction of the filtered solution with chloroform gave only a slight residue, but on standing 48 hr. sulfur was deposited as a yellow gum.

E. **SCN^-, Cl^-, Br^-, I^-, NO_2^-, $S_2O_3^{2-}$, and SO_3^{2-} Salts.**—The absorption at 253 mμ of a 10^{-4} *M* aqueous solution of 3-isothiazolone was unaffected at pH 5.00 by addition of SCN^-, Cl^-, Br^-, I^-, or NO_2^-, indicating the effective absence of nucleophilic attack with ring opening. The addition of SO_3^{2-} led to a rapid rise in the extinction coefficient at 253 mμ, as in the case of CN^-, while the addition of $S_2O_3{}^{2-}$ led to a much slower increase in the specified absorption.

Deuterium Scrambling in the Thiocyanoacrylamide–3-Isothiazolone System.—*cis*-3-Deuterio-3-thiocyanoacrylamide (0.256 g., 0.002 mole, prepared by exchange of propiolamide in D_2O with a trace of potassium carbonate, followed by the usual procedures) was shown by n.m.r. spectroscopy to contain about 82% deuterium on C-3. Microanalysis showed 22.60 atom % D, equivalent to ~90% D on C-3. The material was dissolved in 2 *N* sodium hydroxide (3 ml., 0.006 mole), and 3-isothiazolone (0.202 g., 0.002 mole) was added rapidly. As soon as solution occurred (5 sec.), 2 *N* hydrochloric acid (3 ml., 0.006 mole) was added and the *cis*-3-thiocyanoacrylamide was recovered by chilling and filtration (total elapsed time *ca.* 1 min.). The recovery was 84%. The 3-isothiazolone was then recovered by repeated extraction with chloroform, and the extracts were evaporated at 20°. The n.m.r. spectrum now showed ~41% deuterium on C-5 in this product (corresponding to C-3 in the thiocyanoacrylamide used), confirming that both compounds pass through a common intermediate in alkaline solution. Examination of the recovered *cis*-3-thiocyanoacrylamide by n.m.r. and microanalysis showed exactly the same pattern, *i.e.*, a 50% drop in the deuterium content at C-3. Microanalysis showed 10.90 atom % D, equivalent to ~43% D on C-3.

Equilibrium in the N-Ethyl-3-thiocyanoacrylamide–3-Isothiazolone System.—All solutions were prepared in DMSO-d_6 containing 25% D_2O. Mixtures of (a) *cis*-N-ethyl-3-thiocyanoacrylamide (0.001 *M*) and 3-isothiazolone-5*d* (0.001 *M*) and (b) 2-ethyl-3-isothiazolone and *cis*-3-thiocyanoacrylamide-3*d* were allowed to equilibrate, the product ratios being determined by n.m.r. analysis, using the alkyl group as an internal integration standard. Results were averaged over both solutions when their compositions were experimentally identical (Table I). The equilibrium was approached from both sides to minimize errors. The deuterated compounds were used to facilitate estimation of otherwise overlapping n.m.r. signals.

TABLE I

Typical run (b)	Initial composition	Final composition
cis-3-Thiocyanoacrylamide-3*d*	0.50	0.16
3-Isothiazolone-5*d*	...	0.32
cis-N-Ethyl-3-thiocyanoacrylamide	...	0.36
2-Ethyl-3-isothiazolone	0.50	0.16

$K_{2\text{-Et}}/K_{2\text{-H}} = 0.22 \pm 0.05$ in 75% DMSO-d_6–25% D_2O at *ca.* 25°.

Preliminary Investigation of the Kinetics of Cyclization and Nucleophilic Attack.—The required solvent ($[CN^-]$, $[H^+]$) was prepared and an aliquot (1.00 ml., 0.005 *M* solution) was delivered into the appropriate volume of thiocyanoacrylamide solution (49.00 ml., or 49.2 ml. if the aliquot was an ethereal solution) at time zero. Absorption at $\lambda_{253-256}$, depending on the nature of the substituent on nitrogen, was followed on a Cary Model 15 recording spectrophotometer, and ln $(A_t - A_{\mathrm{equil}})$ *vs.* *t* was a straight-line plot through 90% of the reaction. The equilibrium value was redetermined several hours after equilibrium had apparently been attained. The concentration of cyanide ion was based on calculations assuming $K_{\mathrm{HCN}} = 7.2 \times 10^{-10}$.

Novel Conversion of Diphenylcarbodiimide by Sodium Naphthalene

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The reaction of diphenylcarbodiimide with sodium naphthalenide complex was studied. Several products are formed depending upon experimental conditions, including N,N′,N″,N‴-tetraphenyloxamidine, 1,3-diphenyl-2,4,5-(triphenylimino)imidazolidine, N-(N′,N″-diphenylguanyl)diphenylformamidine, and β-diphenylcarbodiimide. The reaction mechanism evidently involves, as an initial step, the transfer of one or two electrons from sodium naphthalene to the carbodiimide molecule.

It is well known that alkali metals readily combine with some aromatic hydrocarbons in certain basic solvents to form stable colored complexes. Since the earlier work done by Schlenk,[2] several examples of reactions on this kind of organometallic compounds have been reported; for instance, the reaction with carbon dioxide,[3] alkyl halides,[4] and ethers,[5] and the metallation of hydrocarbons[5] and nitriles.[6] Recently they have been used as anionic initiators of polymerization for numerous vinyl compounds.[7] We report here a

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[2] (a) W. Schlenk, *Ann.*, **463**, 1 (1928); (b) *ibid.*, **463**, 281 (1928); (c) *ibid.*, **464**, 22 (1928).

[3] J. F. Walker and N. D. Scott, *J. Am. Chem. Soc.*, **60**, 951 (1938).

[4] H. V. Carter, B. J. McClell, and E. Warhurst, *Trans. Faraday. Soc.*, **56**, 343 (1960); E. Müller and G. Roscheisen, *Chem. Ber.*, **90**, 543 (1957).

[5] J. Eisch and W. Kaska, *Chem. Ind.* (London), 470 (1961).

[6] L. Horner and H. Gusten, *Ann.*, **652**, 99 (1962).

[7] M. Szwarc, *Nature*, **178**, 1168 (1956); M. Szwarc, M. Levy, and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956); H. Brody, M. Ladacki, R. Milkovitch, and M. Szwarc, *J. Polymer Sci.*, **25**, 221 (1957); H. W. McCormick, *ibid.*, **36**, 341 (1959); R. K. Graham, D. L. Dunkelburger, and E. S. Cohn, *ibid.*, **42**, 501 (1960); P. Claes and G. Smets, *Makromol. Chem.*, **44**, 212 (1960); R. K. Graham, J. R. Panchek, and M. T. Kamph, *J. Polymer Sci.*, **44**, 411 (1960).

TABLE I

ANALYTICAL DATA OF REACTION PRODUCTS

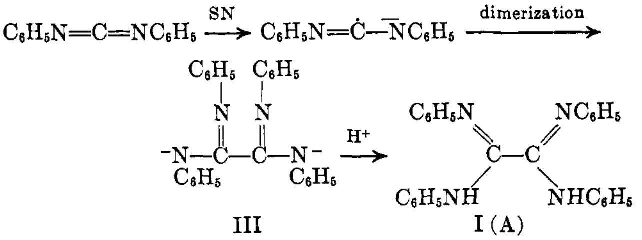
Product	M.p., °C.	$\nu_{C=N}$ (KBr), cm.$^{-1}$	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	Mol. wt. Calcd.	Mol. wt. Found
A	153	1637	$C_{26}H_{22}N_4$	79.97	80.01	5.68	5.85	14.35	14.13	390	...
B	218-218.5	1667	$C_{33}H_{25}N_5$	80.63	80.49	5.13	5.17	14.25	14.29	491	463
C	142.5-143.0	1630, 1647	$C_{26}H_{22}N_4$	79.97	79.98	5.68	5.90	14.35	14.47	390	401
Cyclic dimer of CD			$C_{26}H_{20}N_4$	80.38	...	5.19	...	14.42	...	388	...

novel reaction of diphenylcarbodiimide (CD) which is brought about by sodium naphthalene (SN).

Carbodiimides contain a cumulated double-bond system and suffer attack by nucleophiles in much the same manner as isocyanates and ketenes. It has been found in recent years that isocyanates[8] and ketenes[9] can be polymerized to linear high polymers through the opening of C=N, C=O, or C=C bonds by appropriate catalysts, but a similar type of polymerization has not yet been reported in the case of carbodiimides.[10] Carbodiimides, especially those of aromatic series, are likely to polymerize to cyclic dimers or trimers,[11] although some of their structures are uncertain. For instance, CD is gradually converted to a solid trimer (β-diphenylcarbodiimide), m.p. 158–159°, on standing; in this reaction metallic sodium shows some promoting action.

Interaction of CD with a catalytic amount of SN failed to produce a high polymer even at a low temperature, and the sole product obtained was the β-trimer.[12] By increasing the amount of SN, however, the formation of the β-trimer was significantly suppressed; when the molar ratio of SN to CD was over 0.5, no β-trimer was obtained and three compounds shown in Table I were isolated from the reaction products. The reaction was carried out in tetrahydrofuran at temperatures between −78 and 20° with varying ratios of SN to CD. The total yield of the compounds (A, B, and C) was generally 80–95% by weight of CD used, but their proportion varied remarkably with SN–CD ratio, while temperature dependence was found much less within the range mentioned above. Analyses revealed their formulas as approximately $(C_{13}H_{11}N_2)_n$, in which n is 2 in A and C and about 2.5 in B, suggesting that they are "dimers" or have nearly the same degree of oligomer of CD and do not contain the naphthalene nucleus. In the infrared B exhibited no NH absorption band and may have a cyclic structure, while A and C each showed a strong NH band and could be noncyclic. C is far more basic than the other two and was usually isolated as an acetate when the reaction was stopped with acetic acid.

Compound A was shown to be N,N′,N″,N‴-tetraphenyloxamidine (I) from spectral data and acid hydrolysis to oxanilide (II). The formation of I involves C–C coupling between two molecules of CD, which presumably occurs by electron transfer from the sodium naphthalenide radical anion to the carbodiimide as in the polymerization of styrene with this initiator. In the present case the dianion III would be formed by dimerization, and, if the rate of propagation and the molar ratio of CD to SN are low, the reaction would be largely interrupted at this step with formation of I. The formation of an oxalic acid derivative from phenyl isothiocyanate by the action of disodium tetraphenylethylene[2a] or sodium phenylbiphenyl ketone[2c] presumably also occurs by electron transfer and radical anion dimerization.

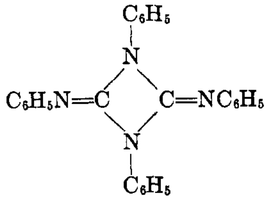


$C_6H_5N{=}C{=}NC_6H_5 \xrightarrow{SN} C_6H_5N{=}\dot{C}{-}\bar{N}C_6H_5 \xrightarrow{\text{dimerization}}$

III

I (A)

The composition of product B was intermediate between that of a dimer and trimer of CD; the compound showed strong C=N absorption at 1667 cm.$^{-1}$ but no NH band. The cyclic dimer IV would be expected to show C=N absorption near 1690 cm.$^{-1}$ [13];



IV

moreover, this structure is unlikely because of the lack of reactivity of B to nucleophilic reagents such as amines and alcohols. The compound was soluble in concentrated sulfuric acid, however, to give a deep red solution, which on being poured into water yielded white crystals, m.p. 235.5° (V). V was further hydrolyzed by heating with concentrated hydrochloric acid in ethanol to a second product melting at 203–204° (VI), which could also be obtained directly from B by a similar treatment. Compounds V and VI exhibited carbonyl absorptions at 1773 and 1741 cm.$^{-1}$, respectively, but none in the NH region, indicating that cyclic structures were retained. These products were identified as 1,3-diphenyl-2-phenyliminoimidazolidine-4,5-dione (N,N′-oxalyltriphenylguanidine) and 1,3-diphenylparabanic acid (N,N′-oxalyldiphenylurea) by com-

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(8) V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Am Chem. Soc.*, **82**, 866 (1960); G. Natta, J. DiPietro, and M. Cambini, *Makromol. Chem.*, **56**, 200 (1960).

(9) G. Natta, G. Mazzanti, G. F. Pregaglia, M. Binaghi, and M. Peraldo, *J. Am. Chem. Soc.*, **82**, 4742 (1960); *Makromol. Chem.*, **44**, 537 (1961); **51**, 148 (1962); R. H. Hasek, R. P. Clark, E. V. Eelan, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962); G. F. Pregaglia, M. Binaghi, and M. Cambini, *Makromol. Chem.*, **67**, 10 (1963).

(10) After this manuscript had been completed, G. C. Robinson [*J. Polymer Sci.*, **A2**, 3901 (1964)] reported success in the polymerization of various carbodiimides.

(11) H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953).

(12) In this paper the trimer of diphenylcarbodiimide (m.p. 158–159°), frequently described as β-diphenylcarbodiimide in earlier literatures, is designated as "β-trimer." Another cyclic trimer, m.p. 196°, is also known and usually refered to as hexaphenylisomelamine. These two are probably geometrical isomers, but definite configurations are uncertain.

(13) F. Zetsche, *Ber.*, **73**, 1123 (1940).

Chart I

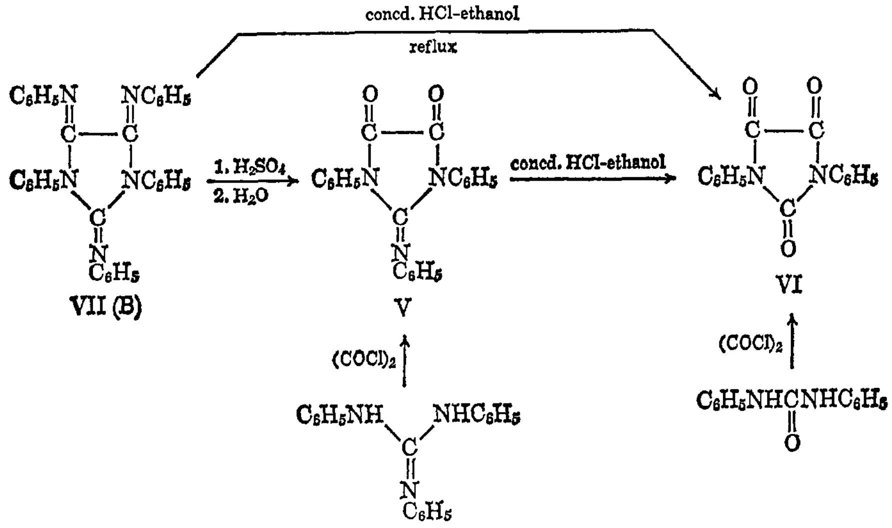
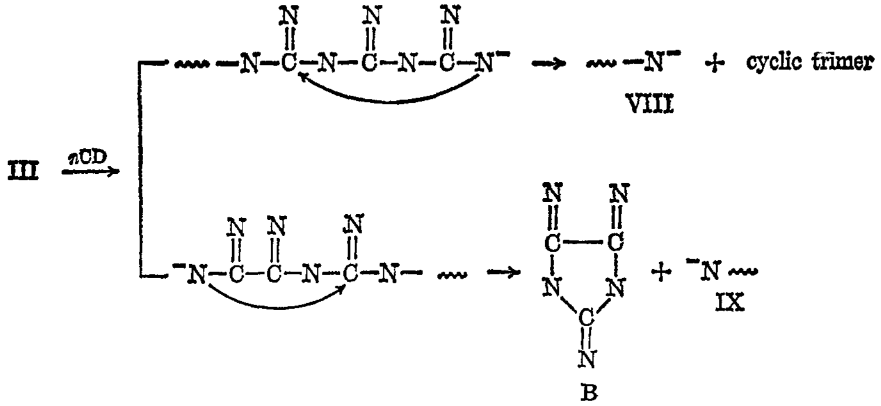


Chart II



(phenyl groups attached to N are neglected)

parison with authentic samples. On the basis of these structures, we came to the conclusion that B was best interpreted as being 1,3-diphenyl-2,4,5-tri(phenylimino)imidazolidine (VII) (Chart I).

As stated earlier, it is assumed that a dianion III would be formed in the initial step of the reaction. When a large amount of CD is present in the system, it will add to III at both active ends, and there seems to be a possibility that a linear high polymer could result. Actually, the cyclization appears to take place preferentially, releasing the cyclic trimer from the chain end, presumably owing to the slower rate of propagation. Addition of the unreacted CD to the regenerated anion VIII and elimination of a second trimer would occur in succession and the main reaction product might be the β-trimer, but another type of cyclization could arise in this case, especially in an earlier stage of propagation through which a second cyclic compound, involving the skeleton of the starting dianion III, might be isolated. In this scheme, the formation of B under proper conditions may be understood as shown in Chart II. It is to be noticed that an unusual type of oligo cyclization is presented here, in which a part of the monomer skeleton becomes partially included in the ring system, leaving the other half in the propagating chain. The departed N-anion IX could again propagate with additional monomer, if present, and yield probably β-trimer, but B could no longer be formed from this species. If these postulations are correct, use of smaller amounts of SN would favor the formation of the trimer, while interaction of about equimolar quantities of SN and CD would enhance the yield of A, and B would be generated under intermediate conditions. In addition, in view of the high rate of reactions, the rate and order of adding reagents would also be expected to have an important effect on the proportion of these products. This is just what we found, and the results are summarized in Table II. The amounts of A and B were measured spectrophotometrically, with the absorptions at 1320 in A and 1380 cm.$^{-1}$ in B as the key bands (Figures 1 and 2).

The mechanism stated above postulates the stoichiometry for the formation of A and B as follows. The

$$2\text{SN} + 2\text{CD} = \text{A}$$

$$2\text{SN} + 3\text{CD} = \text{B}$$

yields of A and B in Table II are based on this scheme; the total yield of A plus B should not exceed 100% theoretically, because these two originate from the same parent species III, while the trimer is free from such restriction. The results obtained are not sufficient for quantitative interpretation because of lack of a precise method of separation and analysis, but the pattern set by the reactions supports the above-

TABLE II

REACTION PRODUCTS BETWEEN CD AND SN UNDER VARYING CONDITIONS[a]

Rate of adding CD	Molar ratio SN–CD	Total yield, g.	β-Trimer, g.	Product				
				A		B		A + B
				g.[b]	%/SN[c]	g.[b]	%/SN[c]	%/SN
Slow[d]	1:1	2.2	...	1.9	63	...	..	63
Slow	1:2	2.5	...	1.05	70	0.7	37	107
Slow	1:3	2.9	1.6	0.7	70	0.5	39	109
Rapid[e]	1:1	2.3	...	0.55	18	1.4	47	65
Rapid	1:2	2.2	...	0.25	17	1.2	63	80
Rapid	1:3	2.2	1.0	0.25	25	0.9	71	96

[a] The reaction was carried out at 0° following the general procedure described in the Experimental part. [b] Calculated from the % content of A or B in the benzene soluble portion, determined spectrophotometrically. [c] Calculated upon basis of the stoichiometric relations presented above. [d] CD was added dropwise as slowly as possible during about 1 hr. [e] CD was added in one portion.

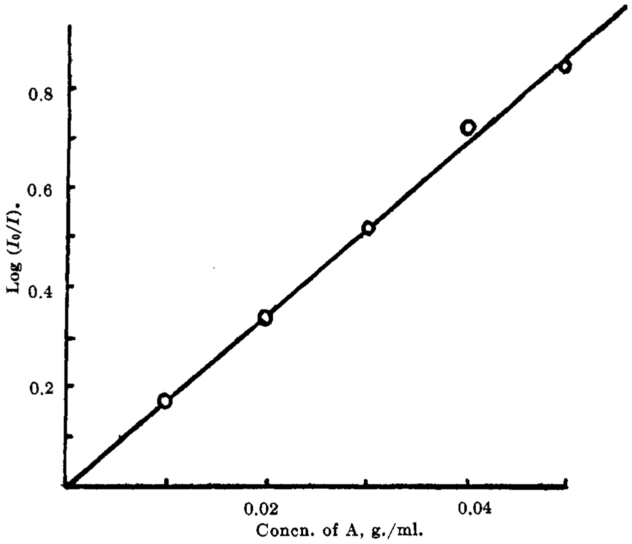


Figure 1.—Calibration curve for A.

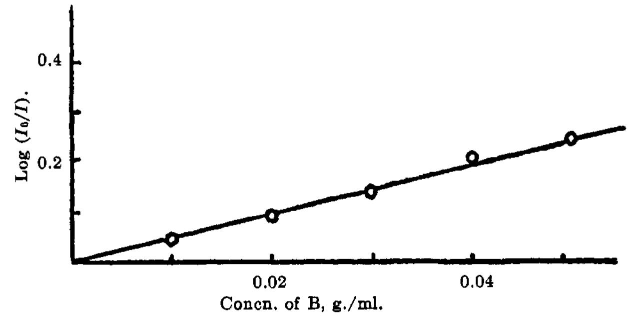
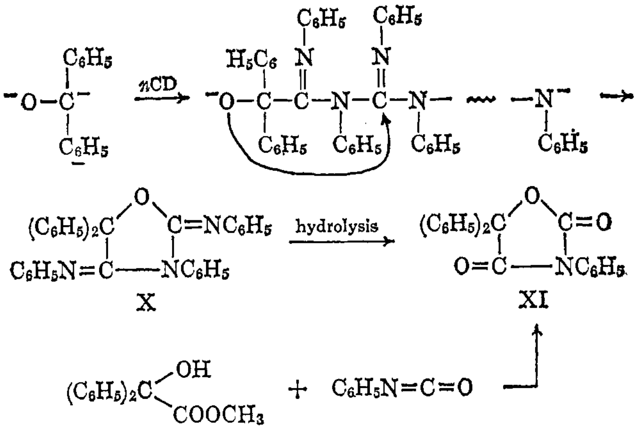


Figure 2.—Calibration curve for B.

mentioned view. It is to be noted here that the total yield of A plus B becomes far less than the calculated one with increasing quantity of SN, in spite of a decrease in the amount of the β-trimer formed. It is mainly due to a third course of reaction described later.

Evidently, SN is acting as a potential source of electrons in these reactions, and the apparent initiating species is the dianion III. If a suitable dianion capable of reacting with CD were selected as initiator in place of SN, it is expected that a cyclic compound which contains the skeleton of the initiator might be obtained. This was demonstrated when disodium benzophenone was employed. The reaction of this initiator with CD turned out to be more complicated and showed results with low reproducibility, but often led to isolation of colorless needles melting at 149.5–150.5° (X). Analyses revealed the formula $C_{33}H_{25}N_3O$ and the absence of NH, again indicating a cyclic structure. The compound was converted by partial hydrolysis to 3,5,5-triphenyl-2,4-dioxooxazolidine (XI), m.p. 142–143°, which was identified by comparison with an authentic sample. The structure of X is thus established as 3,5,5-triphenyl-2,4-diphenyliminooxazolidine (Chart III).

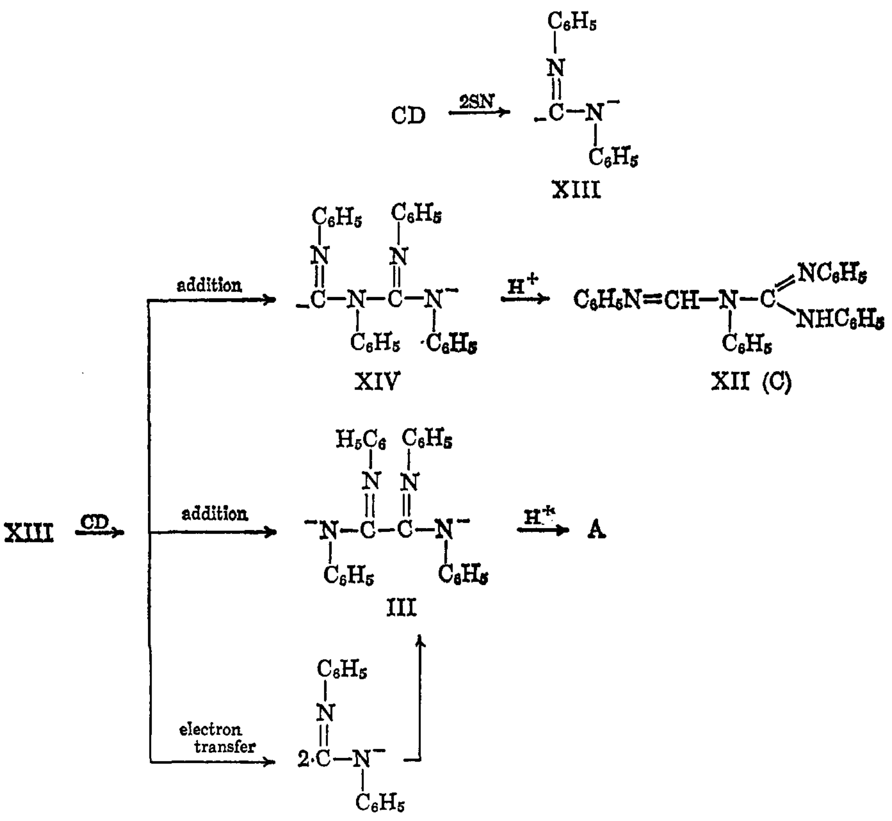
CHART III



Finally, the product C may also be a noncyclic dimer of CD, isomeric with A. In the reaction of CD with excess SN, C was obtained in about 60% yield, and its formation is considered the main cause of the low value in the total yield of A plus B under the conditions of high SN–CD ratio (Table II). Compound C showed two absorption bands at 1647 and 1630 cm.$^{-1}$, possibly associated with two different kinds of C=N. Furthermore, it is basic enough, compared with A and B, to be isolated as a monoacetate, m.p. 172–173°, but the corresponding diacetate was difficult to obtain. This behavior suggested that C contains but one center of basicity, which is strong enough to allow the ready salt formation with weak acids (probably guanidine type). From these observations, compound C was assigned to be N-(N′,N″-diphenylguanyl)diphenylformamidine (XII), despite failure of the attempted synthesis from triphenylguanidine. The probable course of reaction yielding C may be illustrated as shown in Chart IV.

The reaction involves the transfer of two electrons to CD, giving the monomeric dianion XIII. In some aromatic compounds having C=N bonds, addition of two alkali metal atoms has been known to occur.[2b] More familiar examples of a similar type are the reactions of excess sodium with benzophenone or tetraphenylethylene to give the corresponding disodio compounds. In all cases, aromatic substituents are

CHART IV

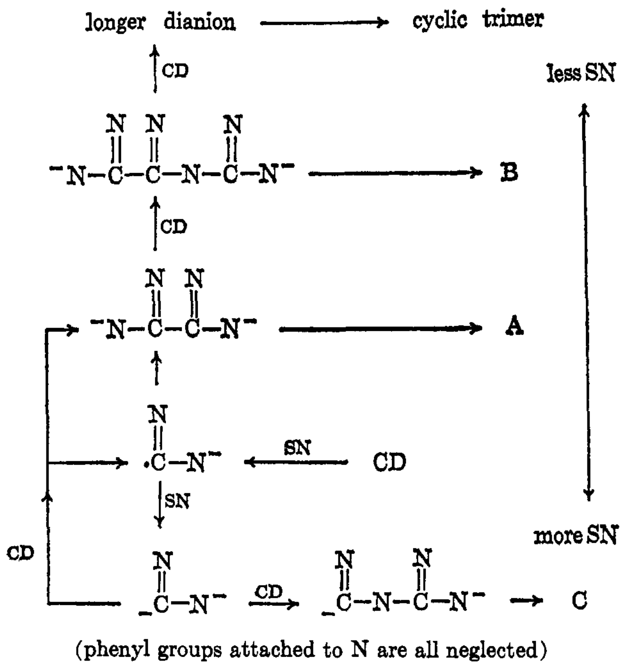


required for the existence of such organometallic compounds. In the present dianion XIII, also, the negative charge which occurs on the central carbon atom would be fairly delocalized over the adjacent $-NC_6H_5$ group, thus facilitating the formation of this dianonic form, but the stability of XIII would probably not be high, and it could react with CD to give a more stable dimeric dianion XIV in which the negative charges are more widely separated than XIII. Since the concentration of CD is very low in this system, there is little possibility of further propagation with XIV, and the product should be XII (C), but the reaction of XIII with CD could occur in another way; the dianion III could also be formed by addition, or electron transfer and radical dimerization, affording the product A.

The outline of the whole reaction between CD and SN is thus summarized in Chart V.

Some additional experiments were carried out with other combinations of analogous compounds. Lithium naphthalene showed some different behavior in the reaction with CD. β-Trimer was formed even with high ratio of SN–CD in the yield of 50–60%, whether CD was added dropwise or in one portion, and the remainder was a tacky mass from which no definite substance could be isolated. The reaction of phenyl isocyanate with SN was also tried in the hope that, under proper conditions, diphenylparabanic acid might be obtained, but gave only N,N′,N″,N‴-tetraphenyloxanilide and triphenyl isocyanurate (cyclic trimer of phenyl isocyanate). In both cases the rate of propagation is possibly too high compared with that of cyclization to permit the formation of this type of cyclic product. On the other hand, phenylmagnesium bromide was found to react with CD only very slowly and yield mainly N,N′-diphenylbenzamidine together with a smaller amount of sirupy material, indicating a very low rate of propagation. Obviously, counter ions are playing an important role, particularly in the propagation step, and the B-type cyclization could only become appreciable within a narrow range of conditions, where a suitable balance in the reaction rates of the various steps was being kept by selection of reagents as well as experimental conditions.

CHART V



(phenyl groups attached to N are all neglected)

Experimental

Diphenylcarbodiimide was prepared from phenyl isocyanate by Campbell's method[14] with 1-phenyl-3-methyl-3-phospholene 1-oxide as catalyst; it was obtained as a colorless oil with b.p. 132–133° (2 mm.).

Reaction of Diphenylcarbodiimide with Sodium Naphthalene (General Procedure).—In a 200-ml. flask, flamed and swept with dry nitrogen, were placed equimolar amounts of naphthalene and sodium (commercially available as a 40% dispersion in paraffin wax). Purified tetrahydrofuran (50 ml., finally distilled over sodium naphthalene immediately before use) was added, and the mixture was stirred at room temperature for 1 hr. and then cooled to 0°. To the deep green solution was added freshly distilled diphenylcarbodiimide (3.0 g., 16 mmoles) through a hypodermic syringe. After a short time the green color of SN vanished and a bright reddish orange solution appeared. The contents were kept at 0° under stirring for 1 hr. and then the reaction was complete in most cases. All these procedures were carried out in a flow of dry nitrogen avoiding contact with air. After neutralization by acetic acid (as solution in tetrahydrofuran), solvent was evaporated under vacuum, and the residue was treated with benzene and water. The insoluble β-trimer was collected and measured. The organic layer was again concentrated under reduced pressure almost to dryness, and the residue was triturated by repeated treatment with n-hexane to remove naphthalene and paraffin. The resulting yellow to reddish orange powder was measured and analyzed spectrophotometrically for A and B as a 5% solution in carbon disulfide. Results are summarized in Table II.

N,N′,N″,N‴-Tetraphenyloxamidine (A).—To the SN solution prepared from 2.0 g. (16 mmoles) of naphthalene and 0.9 g. (16 mmoles) of sodium dispersion, 3.0 g. (16 mmoles) of CD was dropped in as slowly as possible (during 1 hr.). The reaction was otherwise carried out following the general manner described in the above procedure. The yield of crude product was 2.6–2.8 g. and two recrystallizations from cyclohexane raised its melting point to 153–153.5°. No depression was observed in the mixture melting point with the authentic sample,[15] m.p. 153°.

1,3-Diphenyl-2,4,5-tri(phenylimino)imidazolidine (B).—The same amounts of reagents were allowed to react as those shown above, except that CD was added in one portion; the temperature rose temporarily to 10°. After agitating at 0° for 1 hr., the mixture was treated in the same way, yielding 2.5–2.8 g. of orange powder, which consisted largely of B, together with A and the acetate of C. Ten grams of this mixture was extracted with 50 ml. of hot benzene, and the acetate of C was separated after cooling as a white powder, m.p. 165–168° (1.6 g.). From the filtrate was obtained 8.3 g. of a reddish orange mass (m.p. 185–200°), which after two or three recrystallizations from di-n-butyl ether gave pure material as orange prisms, m.p. 218–218.5°.

Hydrolyses of B. 1.—A solution of 5.0 g. of B in 20 ml. of concentrated sulfuric acid was allowed to stand for a few days at room temperature. The deep red solution was poured into ice-water and the precipitated faint yellow solid was collected (3.3 g.). It was recrystallized from benzene and gave 1,3-diphenyl-2-phenyliminoimidazolidine-4,5-dione (N,N′-oxalyltriphenylguanidine) (V) as yellow scales, m.p. 235.5°. No depression in the mixture melting point was observed with the authentic sample, which was prepared by the reaction between N,N′,N″-triphenylguanidine and oxalyl chloride, m.p. 234–235° (lit.[16] *ca.* 230°). In the infrared four peaks were found in the carbonyl region, two strong (1773 and 1700 cm.$^{-1}$) and the others weak (1715 and 1675 cm.$^{-1}$).

Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 74.03; H, 4.42; N, 12.47.

2.—The mixture of 1.0 g. of V, 10 ml. of ethanol, and 5 ml. of concentrated hydrochloric acid was refluxed for 3 hr. On pouring into water there appeared fine needles, which were collected and weighed 0.7 g., m.p. 195–200°. Recrystallization from benzene–hexane gave diphenylparabanic acid (VI) as colorless needles, m.p. 203–204° (lit.[17] 206–207°), infrared absorption 1790 and 1741 cm.$^{-1}$ (for C═O).

Anal. Calcd. for $C_{15}H_{10}N_2O_3$: C, 67.66; H, 3.79; N, 10.52. Found: C, 67.73; H, 3.79; N 10.42.

3.—To the hot suspension of 1.0 g. of B in 10 ml. of ethanol was added 10 ml. of concentrated hydrochloric acid. The contents soon became homogeneous on heating on a steam bath and after a short time fine needles began to separate. After 2 hr. the crystals were filtered off and recrystallized with benzene–hexane. The colorless needles collected weighed 0.5 g. (m.p. 201–203°). Infrared analysis and the mixture melting point determination showed that it was also diphenylparabanic acid.

Reaction of Diphenylcarbodiimide with Disodium Benzophenone (3,5,5-Triphenyl-2,4-di(phenylimino)oxoazolidine, X).—To a mixture of benzophenone (2.9 g., 16 mmoles) and a sodium dispersion (2.75 g., 48 g.-atoms) placed in a dry flask was added 50 ml. of purified tetrahydrofuran under stirring. The reaction was exothermic and external cooling was required to keep the contents under 20°. The initially apparent blue color (associated with the benzophenone radical anion) soon turned to violet and the stirring was continued for 2 hr. Then it was dipped in a cold bath held at 0°, and 3.0 g. (16 mmoles) of CD was added, when the temperature rose temporarily to 10–15°. After 2 hr. of reaction the contents was treated as above, leaving a brownish tacky mass. It was dissolved in hot ethanol and fine crystals, which separated on cooling, were collected by filtration. The yield of crude product, m.p. 143–145°, was 1.3 g. (27%). Two recrystallizations from ethanol afforded pure material as colorless needles melting at 149.5–150.5°: infrared absorptions, 1712 (m), 1675 (s), and 1633 (s) (for C═N), 1211 and 1155 cm.$^{-1}$ (for C–O–C).

Anal. Calcd. for $C_{33}H_{25}N_3O$: C, 82.65; H, 5.25; N, 8.76. Found: C, 82.86; H, 5.41; N, 8.77.

3,5,5-Triphenyl-2,4-dioxooxazolidine (XI).—To the hot solution of X (1.0 g.) in 10 ml. of ethanol was added 10% hydrochloric acid (10 ml.). The initially turbid mixture soon became homogeneous and was refluxed for 3 hr. On cooling, the crude product was separated as needles (m.p 139–140°, 0.4 g.). Recrystallization from ethanol gave long fine needles melting at 142–143°.

Anal. Calcd. for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.29. Found: C, 76.53; H, 4.71; N, 4.25.

It was shown to be identical, by a mixture melting point determination and comparison of infrared spectra (1817 and 1745 for C═O, 1212 and 1189 cm.$^{-1}$ for C–O–C) with the authentic sample, which was obtained from methyl benzilate and phenyl isocyanate by the method of Recker.[18]

N-(N,′N″-Diphenylguanyl)diphenylformamidine (C).—The sodium naphthalene solution was prepared from 3.8 g. of pure naphthalene (30 mmoles), 1.7 g. of a sodium dispersion (30 g.-atoms), and 50 ml. of tetrahydrofuran. After cooling to −50°, 3.0 g. of CD (16 mmoles) was added in one portion, when the temperature rose temporarily to about −35°. On stirring for 1 hr. at −50°, the contents was treated in the similar way as described in the preparation of A, leaving 1.95 g. (56%) of crude acetate of C as a tan powder, m.p. 150–160°. Recrystallization from benzene afforded colorless fine crystals melting at 172–173° dec.: infrared absorptions, 2700 (broad, for amine salt), 1667 (for C=N), 1445, 1400, and 1378 cm.$^{-1}$ (for CH_3-COO^-).

Anal. Calcd. for $C_{28}H_{26}N_4O_2$: C, 74.64; H, 5.82; N, 12.44. Found: C, 74.08; H, 6.02; N, 12.32.

From the ethanolic solution of the acetate was obtained the free base C by neutralization with dilute alkali, which soon precipitated as white solid (almost quantitative); recrystallization from cyclohexane gave pure material as fine needles, m.p. 142.5–143.0°.

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