($CHCl_3$) 1780 (C=O), 1515, 1335 cm^{-1} (NO_2); NMR ($CDCl_3$; Me_4Si external reference) δ 0.25 (s, 9, $SiMe_3$), 2.4 (m, 4, CH_2), 2.6–3.0 (m, 1, CHC(OSiMe$_3$)), 3.6–4.1 (m, 1, CHC=O), 5.85 (m, 2, vinylic), 7.2–8.4 (m, 4, Ar). The material decomposed within a few hours on standing in air. An analytical sample was obtained by recrystallization from Et_2O–pentane (1:8; v/v) at −5 °C, mp 102–3 °C.

Anal. Calcd for $C_{17}H_{21}NO_4SSi$: C, 56.17; H, 5.82; S, 8.82. Found: C, 56.07; H, 5.72; S, 8.78.

Treatment of 7,8-Bis(trimethylsilyloxy)-*cis*-bicyclo[4.2.0]octa-3,7-diene with *tert*-Butyl Hypochlorite. A solution of 5.65 g of **7** and 2.17 g of *t*-BuOCl[22] in 60 mL of spectral grade CCl_4 was irradiated at −45 to −30 °C by means of a GE 275-W sunlamp. After 100 min, the sunlamp was removed, and the solution was warmed to room temperature. Rotary evaporation of the solvent (40 °C) followed by distillation of the residue gave 2.0 g (45%) of **6** as an orange oil, bp 83–85 °C (0.4–0.45 mm), identified by infrared and NMR spectral comparison with an authentic sample prepared as described above.

8-Hydroxybicyclo[4.2.0]oct-3-en-7-one (22). A solution of 14.2 g of **7** in 50 mL of 20% aqueous acetone (v/v) was refluxed under N_2 for 5–6 h, cooled, and extracted with several 30-mL portions of ether. The ether extracts were dried (Na_2SO_4) overnight in a refrigerator, filtered, and rotary evaporated at room temperature to give an oily solid. A solution of the crude solid in 12 mL of ether was cooled in dry ice–acetone for several hours, and the supernatant liquid was decanted. The resulting solid was purified by solution in Et_2O and addition of hexane to the cloud point. Cooling at −20 °C for several hours gave 3.15–3.25 g (43–47%) of **22** as white crystals: mp 59–60 °C; IR ($CHCl_3$) 3595, 3450 (OH), 1775 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.21 (m, 4, CH_2), 2.5–3.3 (m, 2, bridgehead), 3.7 (broad s, shifting with concentration, 1, OH), 4.95 (dd, J = 9.5, 3 Hz, 1, CHOH), 5.7 (m, 2, vinylic). These spectral data agree with those reported by Casadevall and Pouet.[17]

(22) M. T. Mintz and C. Walling, *Org. Synth.*, **49**, 9 (1969).

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **3**, 70355-61-2; **6**, 70355-62-3; **7**, 18014-24-9; **10**, 70355-63-4; **13**, 70355-64-5; **14**, 70355-65-6; **15**, 6383-11-5; **16**, 70355-66-7; **17**, 70355-67-8; **22**, 56402-15-4; *cis*-1,2-dihydroxybenzocyclobutene, 70355-68-9; (*o*-nitrophenyl)sulfenyl chloride, 7669-54-7.

Cycloaddition of Alkynes with *o*-Chloranil: A Route to Halogenated Naphthalenes and Biphenyls

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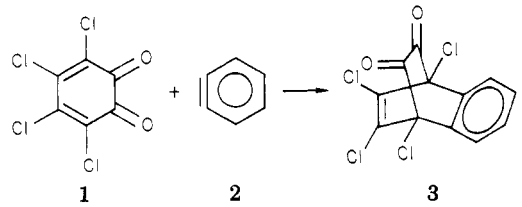
Received October 24, 1978

A synthetic route to chlorinated aromatic glyoxylic acids and analogues has been developed via nucleophilic scission of the α-diketone bridge of the Diels–Alder cycloadducts of *o*-chloranil and alkynes. The adduct of *o*-chloranil and benzyne produced 2,3,4-trichloronaphthalene-1-glyoxylic acid on treatment with aqueous sodium hydroxide. X-ray diffraction confirmed the product structure. The adduct of *o*-chloranil and phenylacetylene produced two glyoxylic acid isomers upon treatment with hydroxide. The major "meta" isomer, 2,3,4-trichlorobiphenyl-5-glyoxylic acid, was separated by fractional recrystallization from the minor "ortho" isomer, 3,4,5-trichlorobiphenyl-2-glyoxylic acid. The latter acid was converted to a trichlorofluorenone upon heating. Both biphenylglyoxylic acids were converted to methyl esters and to known biphenyltrichlorocarboxylates. Applicability of the route to variously substituted halogenated aromatics appears likely.

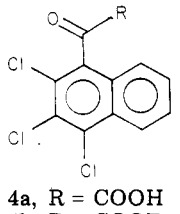
Adducts formed from the Diels–Alder cycloaddition of *o*-chloranil, **1**, and a number of alkynes have been observed



1 **2** **3**

to occur principally across the homodiene. In contrast, cycloaddition with many alkenes occurs across the dicarbonyl.[1] Applications of this reaction in synthesis indicate that the reaction has potential for the formation of chlorinated aromatic systems, including specific isomers of the polychloro- and polybromobiphenyls, although this potential has not been demonstrated. Aromatization and loss of the dicarbonyl bridge by thermal or photolytic action upon adducts such as **3** is the most direct route. A second possibility is nucleophilic attack upon a carbonyl with concomitant ring opening. This course is demonstrated here for the cycloadducts of *o*-chloranil with benzyne and phenylacetylene.

Hydrolysis of the adduct **3**, formed between *o*-chloranil and benzyne, with 5% aqueous sodium hydroxide, produced an aromatic, yellow, crystalline carboxylic acid. The mass spectrum revealed an isotopic pattern for a trichloro derivative, with the largest mass observed at m/e 257. The assignment of the structure **4a** to the product was consistent with the appearance of an acidic ^1H NMR signal and with the formation of the corresponding acylium ion



4a, R = COOH
4b, R = COOEt
4c, R = COOMe
5, R = OMe

(1) L. Horner and H. Merz, *Justus Liebigs Ann. Chem.*, **570**, 89 (1950).

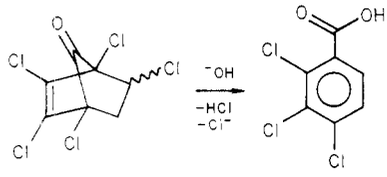
0022-3263/79/1944-2391$01.00/0

(m/e 257) in the mass spectrum. The single-crystal X-ray crystal structure determination confirms the structural assignment of **4a**[2] (see Experimental Section).

The overall yield of **4a** from anthranilic acid (as benzyne precursor) was 53%, the same yield reported for the production of the bridged diketone **3** from anthranilic acid and *o*-chloranil, thereby suggesting that the aromatization is essentially quantitative.[3]

Fischer esterification of **4a** gave the ethyl ester **4b**, which, in contrast to the acid, revealed distinct carbonyl infrared adsorption and a parent ion (m/e 330) in the mass spectrum. The lead tetraacetate oxidation in methanol, an established method of de facto decarboxylation of α-keto acids,[4a] gave the known ester **5**.[4b] The alternate decarbonylation of **4a** to **5** using thionyl chloride,[5] which frequently produces satisfactory decarbonylation of α-keto acids, failed in this case, owing presumably to steric repulsion by ring chlorines to the approach of chloride at the benzylic carbon.

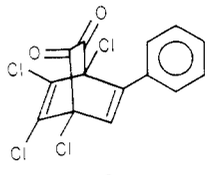
While this is the first report of a simultaneous ring-opening, aromatization reaction upon the bicyclo[2.2.2]-octa-2,5-diene-7,8-dione system, analogous reactions have been observed where an appropriate leaving group at a bridgehead position existed. The norbornenone adduct **6**, arising from cycloaddition of tetrachlorocyclo-



6 7

pentadienenone and vinyl chloride, gives, upon treatment with aqueous ethanol, ring opening with dehydrohalogenation to the acid **7**.[4b] Also, Horner and Merz have observed that Diels–Alder adducts of olefins (e.g., styrene, indene, and 1,3-butadiene) with *o*-chloranil will cleave with loss of chloride when treated with aqueous base.[1]

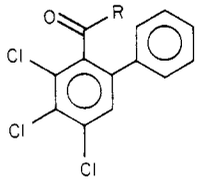
Our results with **3** leading to a naphthalene suggested that the reaction might provide a synthesis of chlorobiphenyls when phenylacetylenes were similarly reacted. The adduct **8** of phenylacetylene and *o*-chloranil, prepared



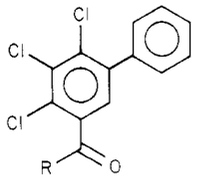
8

by the method of Horner and Merz,[1] yielded two biphenylglyoxylic acids, **9a** and **10a**, in nearly quantitative yield.

Due to thermal instability, it was not possible to distinguish isomers **9a** and **10a** directly by gas chromatography, but conversion to the methyl esters was attempted by treatment with thionyl chloride followed by methanolysis. Unlike the experience with the naphthalene glyoxylate **4a**, the mass spectrum of the methyl ester products **9b** and **10b** showed that some decarbonylation had also occurred, producing about 10% contamination



9a, R = COOH
9b, R = COOMe
9c, R = COOEt
11, R = OMe

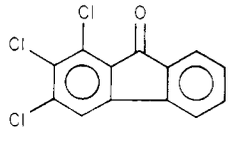


10a, R = COOH
10b, R = COOMe
10c, R = COOEt
12, R = OMe

by the benzoate esters. Ultimately, high-pressure liquid chromatography provided separation, with the products **9a** and **10a** appearing in the ratio of 3:4. Fractional crystallization accomplished isolation of an acid of mp 130.5–132 °C and another of mp 165–166 °C.

The structure assignments were based on differences in the mass spectra. From the higher melting isomer, a molecular ion was observed at m/e 328 showing the expected trichloro isotopic pattern. The relative intensity of this ion decreased dramatically with time, however, indicating that a thermal decomposition was occurring in the inlet of the mass spectrometer. The base peak for each isomer was observed at m/e 283 (loss of CO_2H), assigned as an acylium ion. For the higher melting compound a major peak was also observed at m/e 282 (loss of HCO_2H). The pattern observed for this isomer in the region m/e 282–290 is that expected for two overlapping trichloro-substituted ions.

The peak at m/e 282 is the fluorenone ion **13**, which

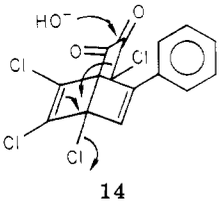


13

requires that the precursor have the phenyl and glyoxylate moieties in an ortho relationship (**9a**). The meta substituted acid **10a** showed no such peak at m/e 282, but there was a metastable peak at that mass owing to the decomposition of m/e 284 to m/e 283. As predicted from the mass spectral result, the acid **9a** produced a known fluorenone, **13**, by thermal decomposition under vacuum sublimation.[6]

The structural assignments for **9** and **10** were further confirmed by conversions to the known[6] methyl carboxylates **11** and **12**, by treatment of **9a** and **10a** with $Pb(OAc)_4$/MeOH, as shown previously for the methyl α-naphthoate **5**.

The ratio of products was found to favor slightly the formation of the meta glyoxylate **10b**, contrary to expectations based on steric hindrance to the attack of hydroxide ion on the adduct **8**. The transition state **14**

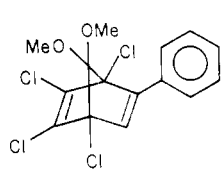


14

depicts a synchronous attack, bridge cleavage, and chloride expulsion leading to the meta product. There appears to be little difference in electronic factors between this route

(2) J. S. Cantrell, R. A. Lunsford, and J. L. Pyle, "Abstracts", American Crystallographic Association, March 1975, H8.
(3) W. Reid and J. T. S. Eng, *Justus Liebigs Ann. Chem.*, **727**, 219 (1969).
(4) (a) E. Baer, *J. Am. Chem. Soc.*, **62**, 1597 (1940); (b) P. Hoch, *J. Org. Chem.*, **26**, 2066 (1961).
(5) J. March, "Advanced Organic Chemistry: Reaction, Mechanisms and Structure", 2nd ed., McGraw-Hill, New York, 1977, p 398.
(6) D. Lemal, E. Gosselink, and S. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966).

and its alternative, but relief of steric strain at the bridgehead nearer the phenyl group may favor the route through **14**. In the case of an analogous decomposition, the norbornadienone dimethyl ketal **15** produced the meta



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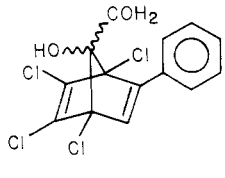

16

isomer of the methyl carboxylate as the dominant product upon pyrolysis.[6] The orientation of ring opening in **8** may also be determined by the existence of an intermediate arising from a normal benzilic acid rearrangement (**16**).

The reaction of a nucleophile with the bicyclooctadienedione system was further tested by reaction of the adduct **8** with sodium methoxide. The reaction produced the methyl glyoxylates **9b** and **10b**, with the meta isomer **10b** dominating again in a ratio of 2.5:1. Methyl esters obtained by the Fischer esterification of pure crystalline glyoxylic acids **9a** and **10a** were used to identify these products which were separated by high-pressure liquid chromatography.

Synthetic Implications

Together with the known photolytic bis decarbonylation previously reported by Strating et al.[7] for **3**, the ring-opening aromatization under nucleophilic attack offers potential for the synthesis of haloaromatic compounds of interest, including halobiphenyls and halonaphthalenes of varying substitution patterns. Synthetic methods leading to halobiphenyls have focused upon the coupling of two aryl systems through arylmetallic precursors or through phenols or diazonium salts.[8] These methods are less useful in the synthesis of the penta-, hexa- and heptachlorobiphenyls, which comprise significant portions of the commercial formulations of interest.

Experimental Section

Anthranilic acid, phenylacetylene, and lead tetraacetate were obtained commercially and used without further purification. o-Chloranil was prepared from pentachlorophenol according to established procedures.[9] Gas chromatography (GC) was performed on a Hewlett-Packard Model 700 chromatograph equipped with thermal conductivity or flame ionization detectors. High-pressure liquid chromatography was performed on a Tracor Chromatec Model 3100 chromatograph, by using a 254-nm ultraviolet absorbance detector and a 4 ft × 9 mm i.d. stainless steel column packed with Chromasep S (nominal 37–44 μm silica gel). Infrared spectra (IR) were obtained with a Perkin-Elmer Model 180 infrared spectrophotometer. Liquid samples were run as thin films between CsI plates, and solid samples were taken as KBr disks. Ultraviolet spectra (UV) were obtained with a Cary Model 14 spectrophotometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6B spectrometer at 70 eV, by using the direct inlet (DI) or vapor–liquid–solid inlet (VLSI). Nuclear magnetic resonance spectra (NMR) were obtained on a JEOL-C-60H spectrometer. Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

2,3,4-Trichloronaphthalene-1-glyoxylic Acid (4a). To a solution of tetrachloro-o-benzoquinone (8.0 g, 32.5 mmol), in 120 mL of p-dioxane and containing 4.8 mL of isoamyl nitrite, was added with stirring half of a solution of 4.42 g (32.2 mmol) of anthranilic acid in 40 mL of p-dioxane over a 15-min period at 60 °C. An additional 4.8 mL of isoamyl nitrite was introduced, and then the remaining anthranilic acid solution was slowly added. The temperature was kept at 60 °C until the evolution of gases had ceased. Eight hundred milliliters of 1 M NaOH was added to the cooled reaction mixture, which was then extracted with three 100-mL portions of ether. Treatment of the ether extract with 50 mL of 5% aqueous NaOH precipitated a light yellow sodium salt of **4a**, which was collected by filtration and washed with 5 mL of dilute base and then with ether. The sodium glyoxylate was suspended in ether and shaken with dilute HCl until the solid dissolved. The separated ethereal layer was washed with a saturated NaCl solution and dried with Na_2SO_4, and then the solvent was flash evaporated. The glyoxylic acid **4a** crystallized from benzene to give 5.2 g (53%) of yellow crystals in two crops: mp 183.5–185 °C; IR (KBr) 1711 cm^{-1}; UV (CH_3OH) 234 (ε 62000), 284 (4500), 293 (4900), 305 (shoulder) nm; NMR (acetone-d_6) δ 9.27 (br s, 1 H, disappears with D_2O), 8.40 (m, 1 H), 7.81 (m, 3 H); mass spectrum (DI) m/e (relative intensity) 302 (10), 257 (100), 238 (15), 229 (30), 194 (52), 159 (16), 147 (10), 123 (15). The single-crystal X-ray structure established the space group to be $P2_1/a$ and the unit cell dimensions as a = 17.199 (10) Å, b = 6.094 (4) Å, c = 12.057 (9) Å, and β = 106.10 (8)°. The unit cell volume is 1214.2 (9) $Å^3$ and the calculated density is 1.664 g/cm^3 (1.68 g/cm^3 observed). There are four molecules per unit cell. The R factor is 0.051 for 1959 reflection data.

Anal. Calcd for $C_{12}H_5Cl_3O_3$: C, 47.49; H, 1.66; Cl, 35.04. Found: C, 47.58; H, 1.68; Cl, 34.93.

Ethyl 2,3,4-Trichloronaphthalene-1-glyoxylate (4b). Compound **4a** (0.50 g, 1.6 mmol) was dissolved in 10 mL of absolute EtOH, and HCl gas was bubbled in with swirling for about 1 min. Much heat was evolved. The vessel was then closed and allowed to cool. After sitting two days, the ester had crystallized and was collected by filtration, yielding 0.52 g (95%) of white crystals: mp 96–96.5 °C; IR (KBr) 1751, 1710 cm^{-1}; UV (CH_3OH) 234 (ε 66000), 283 (4400), 293 (4500) nm; NMR ($CDCl_3$) δ 8.34 (m, 1 H), 7.68 (m, 3 H), 4.44 (q, 2 H, J = 7 Hz), 1.39 (t, 3 H, J = 7 Hz); mass spectrum (DI) m/e (relative intensity) 330 (7), 257 (100), 229 (20), 194 (35).

Anal. Calcd for $C_{14}H_9Cl_3O_3$: C, 50.71; H, 2.74; Cl, 32.08. Found: C, 50.54; H, 2.82; Cl, 32.23.

Methyl 2,3,4-Trichloronaphthalene-1-glyoxylate (4c). Compound **4a** (0.51 g, 1.7 mmol) was reacted with 2.5 mL of thionyl chloride at reflux for 15 min with exclusion of moisture (Drierite). After the solution was cooled, 8 mL of anhydrous MeOH was cautiously added (vigorous reaction) and then the mixture was heated to reflux for 5 min. After flash evaporation of solvent, the pale yellow solid remaining was dissolved in CH_2Cl_2, filtered, and recrystallized from CCl_4 to give 0.35 g (67%): mp 124.5–126 °C; IR (KBr) 1734, 1712 cm^{-1}; UV (CH_3OH) 234 (ε 68000), 282 (4400), 293 (4500), 305 (shoulder) nm; NMR ($CDCl_3$) δ 8.07 (m, 1 H), 7.65 (m, 3 H), 3.98 (s, 3 H); mass spectrum (DI) m/e (relative intensity) 316 (6), 257 (100), 229 (27), 194 (47), 159 (15), 123 (13).

Anal. Calcd for $C_{13}H_7Cl_3O_3$: C, 49.17; H, 2.22; Cl, 33.49. Found: C, 49.02; H, 2.25; Cl, 33.61.

Methyl 2,3,4-Trichloronaphthalene-1-carboxylate (5). Compound **4a** (1.00 g, 3.3 mmol) and 1.86 g (4.2 mmol) of $Pb(OAc)_4$ were quickly weighed into a flask which was then covered with a serum cap. The flask was vented with a syringe needle and 20 mL of a 1:4 MeOH–benzene solution which had been dried over 3A molecular sieves was added. A voluminous precipitate formed immediately. The mixture was heated to 54 °C and the evolution of gas commenced, ceasing after about 30 min, by which time almost all of the precipitate had dissolved. Solid Na_2SO_4 was added to precipitate $PbSO_4$, which was filtered off. The filtrate was treated with $NaHCO_3$ to neutralize acetic acid and any unreacted starting material. Ether and H_2O were added, the mixture was shaken, and the layers were separated. The ether layer was extracted with two additional portions of aqueous $NaHCO_3$, dried with Na_2SO_4, and filtered, and the solvent was flash evaporated. Crystallization from cyclohexane gave 0.66 g (69%): mp 99.5–101.5 °C (lit.[10] mp 96.5–97.5 °C); IR (KBr) 1730

(7) J. Strating, B. Zwanenburg, A. Wagenaar, and A. Udding, *Tetrahedron Lett.*, 125 (1969).

(8) O. Hutzinger, S. Safe, and V. Zitko, "The Chemistry of PCB's", CRC Press, Cleveland, Ohio, 1974, pp 41–63.

(9) A. Rocklin, U. S. Patent 2920082; *Chem. Abstr.*, **54**, 10959i (1960).

(10) P. Ranken and M. Battiste, *J. Org. Chem.*, **36**, 1996 (1971).

cm^{-1}; UV (CH_3OH) 236 (ε 73 000), 283 (5100), 294 (6900), 304 (5000) nm; NMR ($CHCl_3$) δ 8.28 (m, 1 H), 7.67 (m, 3 H), 4.12 (s, 3 H); mass spectrum (DI) *m/e* (relative intensity) 288 (57), 257 (100), 229 (27), 194 (42), 159 (15), 123 (14).

Anal. Calcd for $C_{12}H_7Cl_3O_2$: C, 49.78; H, 2.44; Cl, 36.73. Found: C, 49.74; H, 2.60; Cl, 36.50.

3,4,5-Trichlorobiphenyl-2-glyoxylic Acid (9a) and 2,3,4-Trichlorobiphenyl-5-glyoxylic Acid (10a). *o*-Chloranil (23.8 g, 96.8 mmol) and phenylacetylene (15.4 g, 151 mmol) were maintained at reflux in 240 mL of benzene for 24 h. The solution was then cooled and treated with slow addition of 200 mL of a 2 M NaOH solution, with vigorous stirring, and then allowed to cool overnight. The crystalline sodium salts of the acidic products were washed with 30 mL of dilute aqueous NaOH and then with several portions of benzene. The salts were dried under vacuum to a weight of 33.6 g (98.7% crude yield). Dilute HCl and ether were added to produce the acids, which were soluble in the ether layer. The aqueous layer was reextracted with ether, and the combined ethereal solutions were washed with saturated aqueous NaCl, dried with Na_2SO_4, and filtered; then solvent was flash evaporated. Addition of cyclohexane induced solidification giving 29.6 g (92.9%) of the crude, mixed acids. High-pressure liquid chromatography of the mixture using 1.5% acetic acid in ether as the eluant gave a chromatogram whose relative peak areas were comparable to those from a known 1:1.3 **9a** to **10a** mixture of the acids. The solid was dissolved in 200 mL of hot benzene and allowed to cool, yielding 4.5 g of the crude **9a**. Two recrystallizations from benzene yielded an analytical sample of white, microcrystalline **9a**, which slowly turned yellow when exposed to light: mp 165–166 °C; IR (KBr) 1747, 1711 cm^{-1}; UV (CH_3OH) 207 (ε 39 000), 245 (18000) nm; NMR (acetone-d_6) δ 5.9 (br s, 1 H, disappears with D_2O), 7.73 (s, 1 H), 7.44 (m, 5 H); mass spectrum (DI) *m/e* (relative intensity) 328 (5), 283 (100), 248 (13), 220 (40), 184 (15), 150 (29); high-pressure liquid chromatography (1.5% (v/v) CH_3COOH in anhydrous ether) *k'* 1.7.

Anal. Calcd for $C_{14}H_7Cl_3O_3$: C, 51.02; H, 2.14; Cl, 32.27. Found: C, 51.20; H, 2.30; Cl, 32.09.

Evaporation of the benzene from the mother liquor followed by dissolution in 400 mL of hot cyclohexane yielded approximately 13.5 g of the crude meta isomer **10a** upon cooling. Recrystallization from 150 mL of hot CCl_4 gave 8.84 g; mp 130.5–132 °C. An additional recrystallization yielded **10a** in fine, white needles: mp 131.5–133 °C; IR (KBr) 1708 cm^{-1}; UV (CH_3OH) 207 (ε 39 000) nm; NMR (acetone-d_6) δ 8.7 (br s, 1 H, disappears with D_2O), 7.73 (s, 1 H), 7.53 (m, 5 H); mass spectrum (DI) *m/e* (relative intensity) 328 (14), 283 (100), 220 (82), 184 (15), 150 (46); high-pressure liquid chromatography (1.5% (v/v) CH_3COOH in anhydrous ether) *k'* 3.4.

Anal. Calcd for $C_{14}H_7Cl_3O_3$: C, 51.02; H, 2.14; Cl, 32.27. Found: C, 50.85; H, 2.18; Cl, 32.24.

1,2,3-Trichloro-9-fluorenone (13). An attempt to purify **9a** by vacuum sublimation resulted in decomposition with evolution of a gas, giving an intense, yellow crystalline compound as the sublimate, beginning at approximately 120 °C (0.05 mmHg) and progressing rapidly at 140 °C. The sublimate was dissolved in benzene, washed with several portions of aqueous $NaHCO_3$ to remove acidic material, dried with Na_2SO_4, filtered, concentrated, and allowed to crystallize. Two recrystallizations from benzene gave fibrous, yellow crystals: mp 233–234 °C (lit.[6] mp 233–234.5 °C); IR (KBr) 1712 cm^{-1}; UV (CH_3OH) 215 (ε 28 000), 259 (45 000), 268 (78 000), 292 (2800), 303 (3100), 311 (shoulder), 318 (1900), 335 (1200) nm; mass spectrum (DI) *m/e* (relative intensity) 282 (100), 254 (16), 219 (13), 184 (39), 149 (13).

Anal. Calcd for $C_{13}H_5Cl_3O$: C, 55.07; H, 1.78; Cl, 37.51. Found: C, 55.18; H, 1.85; Cl, 37.32.

Methyl 3,4,5-Trichlorobiphenyl-2-carboxylate (11). The procedure was the same as for the preparation of **5** except that 1.03 g (3.1 mmol) of the glyoxylate **9a** and 1.47 g (3.3 mmol) of $Pb(OAc)_4$ were used. There was no precipitate other than undissolved $Pb(OAc)_4$, and the reaction was completed in 15 min. Similar workup, using MeOH for the crystallization, yielded 0.34 g (34%) of colorless, diamond-shaped plates: mp 59–60 °C (lit.[6] 58–60 °C); IR (KBr) 1738 cm^{-1}; UV (CH_3OH) 208 (ε 41 000), 255 (shoulder) nm; NMR ($CDCl_3$) δ 7.38 (m, 6 H), 3.69 (s, 3 H); mass spectrum (DI) *m/e* (relative intensity) 314 (42), 283 (100), 248 (10), 220 (53), 184 (16), 150 (34).

Anal. Calcd for $C_{14}H_9Cl_3O_2$: C, 53.28; H, 2.87; Cl, 33.70. Found: C, 53.22; H, 3.00; Cl, 33.57.

Methyl 2,3,4-Trichlorobiphenyl-5-carboxylate (12). The procedure was the same as for the preparation of **11** except that 1.00 g (3.0 mmol) of **10a** and 1.92 g (4.3 mmol) of lead tetraacetate were used. No precipitate was formed and the reaction was complete within 5 min. Similar workup yielded 0.86 g (90%) in three crops from cyclohexane: mp 104–105 °C (lit.[6] 105–106 °C); IR (KBr) 1727 cm^{-1}; UV (CH_3OH) 209 (ε 38 000), 298 (1300) nm; NMR ($CDCl_3$) δ 7.72 (s, 1 H), 7.45 (s, 5 H), 3.95 (s, 3 H); mass spectrum (DI) *m/e* (relative intensity) 314 (79), 283 (100), 220 (76), 184 (15), 150 (42).

Anal. Calcd for $C_{14}H_9Cl_3O_2$: C, 53.28; H, 2.87; Cl, 33.70. Found: C, 53.40; H, 2.92; Cl, 33.56.

Esterification of the Biphenylglyoxylic Acid Mixture 9a and 10a with Thionyl Chloride Followed by Methanol. *o*-Chloranil (4.84 g, 19.7 mmol) was reacted with 5 mL of phenylacetylene for 1.5 h at approximately 50 °C. The solution was cooled to room temperature overnight and then reacted with 50 mL of 1.65 M NaOH. After a few hours, the sodium glyoxylates had crystallized and were collected and washed with 40 mL of benzene in several portions. The solid was shaken with dilute HCl and ether, the layers were separated, and the aqueous layer was extracted with two additional portions of ether. The combined ether extracts were dried with Na_2SO_4, filtered, and concentrated to yield 6.5 g (100%) of the crude glyoxylic acids. Thionyl chloride, 10 mL, was added to the solid and the mixture brought to reflux for 30 min with the exclusion of moisture (Drierite). After the mixture was cooled, 25 mL of reagent MeOH was cautiously added, followed by reflux for 15 min. The methanolic solution was diluted with water and extracted with ether. The ether extract was washed with dilute $NaHCO_3$, dried with Na_2SO_4, and concentrated to give 6.70 g of a yellow oil. Analysis by gas chromatography, and mass spectrometry of collected fractions, revealed four products. The first two components to elute were minor products (10% of the total flame ionization detector (FID) peak area), the methyl trichlorobiphenylcarboxylates **11** and **12** resulting from decarbonylation and esterification: **11**, $r_{n\text{-}C_{22}}$ (Dexsil 400, 200 °C) 1.9; mass spectrum (VLSI) *m/e* (relative intensity) 314 (35), 283 (100), 220 (56), 184 (19), 150 (41). **12**, *r* 2.9; mass spectrum (VLSI) *m/e* (relative intensity) 314 (51), 283 (100), 220 (68), 184 (22), 150 (44). The major products (90%) were glyoxylate esters **9b** and **10b**: **9b**, *r* 3.3; mass spectrum (VLSI) *m/e* (relative intensity) 342 (2), 314 (6), 283 (100), 248 (12), 220 (58), 184 (17), 150 (36). *r* 4.9; mass spectrum (VLSI) *m/e* (relative intensity) 342 (4), 314 (1), 283 (100), 220 (63), 184 (13), 150 (36).

Methyl 3,4,5-Trichlorobiphenyl-2-glyoxylate (9b). The acid **9a** (1.00 g, 3.0 mmol) was weighed into a 50-mL flask which was then sealed with a serum cap. Absolute MeOH was dried over 3A molecular sieves and then 10 mL was added to the flask by syringe. The flask was vented with a syringe needle and HCl was introduced through the cap until the solvent began to reflux from the heat of solution. After standing overnight, the solution was neutralized with saturated aqueous $NaHCO_3$ and extracted with several portions of ether, and the combined ether extracts were washed with dilute $NaHCO_3$, dried with Na_2SO_4, filtered, and concentrated by flash evaporation. Crystallization from cyclohexane yielded 0.90 g (86%) in two crops; mp 79.5–84 °C. Recrystallization twice from cyclohexane gave colorless needles: mp 89–90.5 °C; IR (KBr) 1762, 1722 cm^{-1}; UV (CH_3OH) 204 (ε 43 000), 247 (18 000), 310 (shoulder) nm; NMR ($CDCl_3$) δ 7.35 (m, 6 H), 3.68 (s, 3 H); mass spectrum (DI) *m/e* (relative intensity) 348 (2), 283 (100), 248 (11), 220 (51), 184 (13), 150 (27); GC $r_{n\text{-}C_{22}}$ (Dexsil 400, 200 °C) 3.2.

Anal. Calcd for $C_{15}H_9Cl_3O_3$: C, 52.44; H, 2.64; Cl, 30.95. Found: C, 52.36; H, 2.80; Cl, 30.79.

Methyl 2,3,4-Trichlorobiphenyl-5-glyoxylate (10b). The procedure used was identical with that for the preparation of **9b**, from 1.00 g of the acid **10a**. However, all attempts to induce crystallization of the isolated product failed. A portion of the product was distilled under vacuum by using a micro, short-path distillation apparatus. GC analysis of the distillate indicated that 96% of the peak area (FID detection) was due to the desired product, the remainder being distributed among five impurities. The distillate had the following characteristics: bp 200 °C (0.03 mm); IR (film on CsI) 1758, 1739, 1715 cm^{-1}; UV (CH_3OH) 205

(ε 47 000), 247 (12 000) nm; NMR ($CDCl_3$) δ 7.60 (s, 1 H), 7.44 (br, s, 5 H), 3.99 (s, 3 H); mass spectrum (VLSI) *m/e* (relative intensity) 342 (4), 329 (1), 283 (100), 220 (59), 184 (10), 150 (32); GC $r_{n\text{-}C_{22}}$ (Dexsil 400, 200 °C) 4.6.

Anal. Calcd for $C_{15}H_9Cl_3O_3$: C, 52.44; H, 2.64; Cl, 30.95. Found: C, 52.67; H, 2.80; Cl, 31.03.

Because of the impurities evident in the gas chromatogram and the mass spectrum, **10b** was collected by preparative GC. Material collected off SE-52 at 220 °C gave IR and mass spectra essentially identical with the above.

Methyl 3,4,5-Trichlorobiphenyl-2-glyoxylate (9b) and Methyl 2,3,4-Trichlorobiphenyl-5-glyoxylate (10b) Directly from the Diels-Alder Adduct. *o*-Chloranil (1.09 g, 4.4 mmol) was reacted with 1.07 g (10.4 mmol) of phenylacetylene in 30 mL of benzene at reflux for 12 h. After the solution was cooled, 1.20 g of a commercial 25% NaOMe solution in methanol was added. After 5 min, the reaction was quenched with dilute aqueous $NaHCO_3$ and extracted thoroughly with several portions of pentane. The combined pentane extracts were washed with dilute aqueous $NaHCO_3$, dried with Na_2SO_4, and flash evaporated to an oil: 1.48 g (97% crude yield). GC analysis revealed two products comparable in retention times to the methyl esters **9b** and **10b** previously prepared separately. Mass spectrometry of samples collected off the gas chromatograph were identical for **9b** and **10b**. Gas chromatography gave the following: ortho ester **9b**, $r_{n\text{-}C_{22}}$ (Dexsil 400, 200 °C) 3.2, 21% yield; meta ester **10b**, *r* 4.7, 54% yield. Preparative high pressure liquid chromatography using 0.5% MeOH (v/v) in pentane gave the following: ortho ester **9b**, *k'* 1.5, crystallized as colorless plates from cyclohexane, mp 88.5–90 °C (underpressed when mixed with pure **9b**); meta ester **10b**, *k'* 2.9, a slightly yellow oil.

Registry No. 1, 2435-53-2; **4a**, 64253-27-6; **4a** Na salt, 70072-52-5; **4b**, 70072-53-6; **4c**, 70072-54-7; **5**, 29261-09-4; **9a**, 65531-05-7; **9a** Na salt, 70072-55-8; **9b**, 70072-56-9; **10a**, 65242-83-3; **10a** Na salt, 70072-57-0; **10b**, 70072-58-1; **11**, 70072-59-2; **12**, 3258-80-8; **13**, 6453-83-4; anthranilic acid, 118-92-3; phenylacetylene, 536-74-3; *o*-chloranil, 2435-53-2.

Periselective Addition of Mesoionic Compounds to Tetracyanoethylene. Preparation of [(Dicyanovinyl)hydrazono]malononitriles

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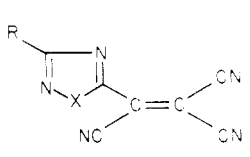
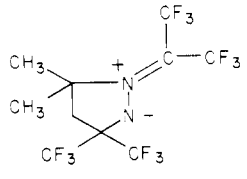
[(Dicyanovinyl)hydrazono]malononitriles are formed in moderate yields when sydnones are heated with tetracyanoethylene in inert solvents. An unstable bicyclic adduct, formed by a periselective 1,3-dipolar addition of the sydnone to the TCNE double bond, is proposed as a reaction intermediate. The [(dicyanovinyl)-hydrazono]malononitriles undergo ready solvolysis under a variety of conditions to yield the corresponding hydrazonomalononitriles.

Tetracyanoethylene (TCNE) reacts with 1,3-dienes to form Diels–Alder adducts,[1] but the mode of cycloaddition to 1,3-dipoles is less predictable. As reported[2] earlier, nitrile sulfides and nitrile oxides react at the nitrile function of TCNE to yield the tricyanoethylenes **1a** and



R = aryl, alkyl

1a, X = S
b, X = O



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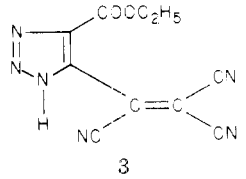

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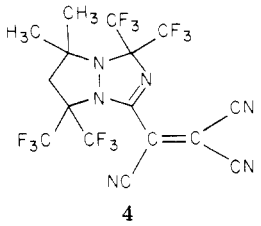

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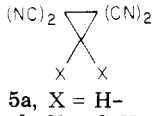
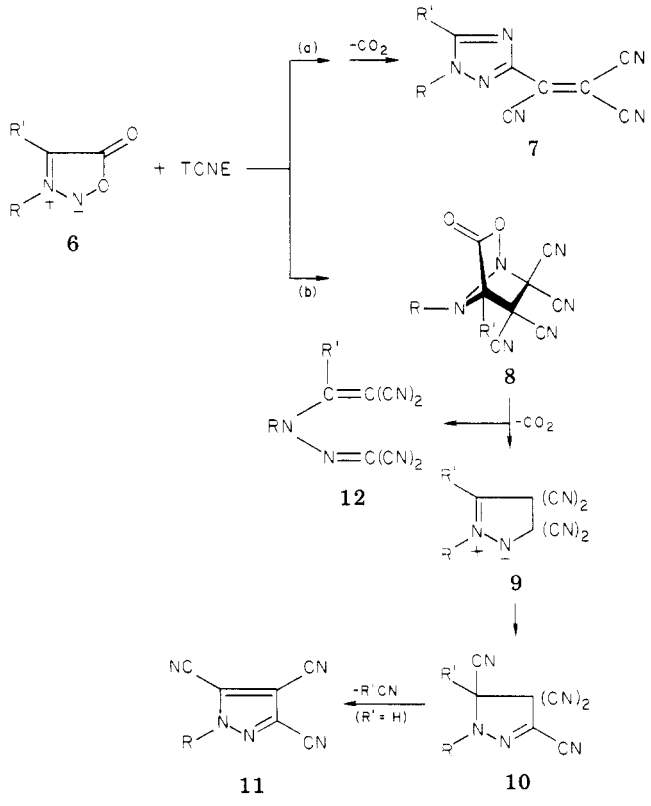


5a, X = H–
b, X = C_6H_5–

Scheme I



6 **7** **8** **9** **10** **11** **12**

1b. Ethyl diazoacetate and the pyrazoline **2** react with TCNE in a similar manner to afford the products **3**[3] and

(1) W. Middleton, R. Heckert, E. Little, and G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).
(2) J. E. Franz, R. K. Howe, and H. K. Pearl, *J. Org. Chem.*, **41**, 620 (1976).

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