continued to reduce the residual AB in the catholyte until the current dropped to 12 mA. The total electrolysis time was 6.0 hr; 0.0243 F had been passed.

A sample of the catholyte was directly analyzed by glc for **30** and **29** using *m*-xylene as an internal standard. The catholyte was then poured onto ice and extracted three times with CH_2Cl_2. The combined extracts were washed and dried over $MgSO_4$. The filtered solution was stripped of low-boiling components on a rotary evaporator using an aspirator and warm-water bath. The residue (10.0 g) was examined by glc for **32** using an authentic reference sample and then analyzed quantitatively using ethyl benzoate as an internal standard.

Reaction of Diethyl Malonate with Ethyl Trichloroacetate.—To 50 ml of pure DMF contained in a four-necked 500-ml flask equipped with thermometer, mechanical Trubore stirrer, and drying tube was added 2.2 g (0.05 mol, dry basis) of 54.7% sodium hydride (Metal Hydrides). Then 16.0 g (0.10 mol) of diethyl malonate was added slowly while the temperature was kept below 40° by cooling in an ice-water bath. When hydrogen evolution had ceased, a clear, very pale yellow solution resulted. This was further cooled and then 9.6 g (0.05 mol) of ethyl trichloroacetate was added in 10 min with vigorous stirring at a temperature of 27°. Turbidity appeared a few minutes after addition was complete. Stirring was continued (arbitrarily) for 5 hr at room temperature. The mixture was poured onto 200 g of ice (alkaline solution) and extracted twice with 50-ml portions of CH_2Cl_2. The combined extracts were washed twice with water, dried over $MgSO_4$, filtered, and warmed on a hot water bath to expel CH_2Cl_2. The residual liquid (24.0 g) was analyzed by glc and found to contain (in order of elution) (a) ethyl dichloroacetate (3.2 g), (b) ethyl trichloroacetate (0.42 g), (c) diethyl malonate (6.3 g), (d) diethyl chloromalonate (5.1 g), and (e) tetraethyl ethane-1,1,2,2-tetracarboxylate (3.2 g). A sample of d was collected by preparative glc. Its nmr spectrum ($CDCl_3$) showed δ 4.83 (1 H, s, CH), 4.29 (4 H, q, 2 CH_2), and 1.34 (6 H, t, 2 CH_3) and was virtually identical with Sadtler Spectrum No. 1880 for the bromo analog.

In another similar experiment e was collected by distillation at 125–139° (0.25 mm). The product solidified in the receiver. After crystallization from ethanol, it melted at 75–76°, undepressed when admixed with authentic material.

Registry No.—**6b**, 20101-80-8; **7**, 25335-12-0; **8**, 34405-06-6; **9**, 34405-07-7; **10**, 34405-08-8; **17a**, 34405-09-9; **17b**, 34405-10-2; *cis*-**18a**, 34405-11-3; *trans*-**18a**, 34405-12-4; *cis*-**18b**, 34405-13-5; *trans*-**18b**, 34405-14-6; **19**, 34405-15-7; BC, 100-44-7; BBN, 5332-06-9; CAN, 107-14-2; CF, 67-66-3; CT, 56-23-5; EBA, 105-36-2; EBB, 2969-81-5; ETA, 515-84-4; AN, 107-13-1; CO_2, 124-38-9; DEF, 623-91-6; DEM, 141-05-9; EA, 140-88-5; AB, 106-95-6; AC, 107-05-1.

Acknowledgment.—We wish to thank Dr. John H. Wagenknecht for discussions on polarographic results, Dr. Pierre A. Berger for detailed nmr analysis of **17b**, and Clarence Robb for preparing an authentic sample of **10**.

Oxidative Carbon–Carbon Coupling. II. The Effect of Ring Substituents on the Oxidative Carbon–Carbon Coupling of Arylmalonic Esters, Arylmalonodinitriles, and Arylcyanoacetic Esters

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Arylmalonic esters and arylmalonodinitriles can be coupled oxidatively to the corresponding bibenzyls. Good yields of dimers are obtained when a para substituent (CH_3, Cl) is introduced, which inhibits the formation of higher oligomers through benzylic C–para C coupling. Substitution at *both* ortho positions and the para position (CH_3) in phenylcyanoacetic esters completely inhibits C–C coupling by steric crowding. Ketene imines are formed instead by C–N coupling. Substitution at *one* ortho position (CH_3) partially gives the usual C–C coupling together with benzylic C–para C coupling (oligomer formation) in case of a free para position and C–N coupling (ketene imine formation) in case of a CH_3-substituted para position. The thermal dissociation of the dimers into radicals is confirmed by esr analysis. From nmr line width measurements kinetic parameters for the dissociation reaction are obtained.

The oxidation of benzyl cyanides, α substituted with ester, acyl, or amide groups to give high yields of C–C dimers, has been described in the previous paper.[1] On thermal treatment the C–C dimers showed a reversible radical dissociation–recombination attended with oligomerization *via* benzylic C–para C coupling in the case of free para positions. Attempts to extend this oxidative dimerization reaction to unsubstituted phenylmalonic esters failed; only low yields of dimers were obtained, presumably owing to formation of higher oligomers. The present paper describes the oxidation of para-substituted arylmalonic esters and arylmalonodinitriles. The effect of both *o*- and *p*-CH_3 substituents on the oxidative coupling of arylcyanoacetic esters is also reported.

Arylmalonic Ester 1a–c.—The oxidation of **1a–c** has been carried out at room temperature with $KMnO_4$, $K_3Fe(CN)_6$, and $[Cu(OH)(TMEDA)]_2Cl_2$-oxygen (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) (*cf.* Table I).

With the first two oxidants, the C–C coupled dimers **2b** and **2c** were formed in high yield, whereas dimer **2a** was only produced as a minor product. In agreement with these results the oxidation of diester **1a** with dibenzoyl peroxide at 100° (neat) has been reported to give only 10% of dimer **2a**.[2] From gel permeation

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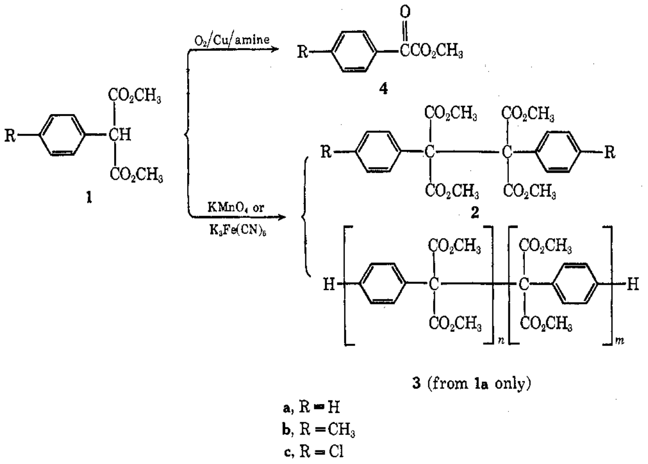
[1] H. A. P. de Jongh, C. R. H. I. de Jonge, and W. J. Mijs, *J. Org. Chem.*, **36**, 3160 (1971).

[2] T. Suehiro, *Nippon Kagaku Zasshi*, **79**, 457 (1958); *Chem. Abstr.*, **54**, 4486*g* (1960).

TABLE I

PROPERTIES AND YIELDS OF DIMERS 2

Dimer	Oxidant	Solvent	Yield, %	Mp, °C
2a	$KMnO_4$	Acetone/NH_3	10	191–192.5
2a	$K_3Fe(CN)_6$	Aqueous NaOH/CH_2Cl_2	11	
2a	O_2/Cu/amine	Methanol	3.4	
2b	$KMnO_4$	Acetone/NH_3	80	161.1–161.7
2b	$K_3Fe(CN)_6$	Aqueous NaOH/CH_2Cl_2	81	
2b	O_2/Cu/amine	Methanol	13	
2c	$KMnO_4$	Acetone/NH_3	68	167.5–169.5
2c	$K_3Fe(CN)_6$	Aqueous NaOH/CH_2Cl_2	78	



chromatography measurements it followed that about 40% of the oxidation product of **1a** (oxidized with $KMnO_4$) was trimer with about 10% of tetramer, presumably formed by a combination of benzylic C–benzylic C and benzylic C–para C coupling. The structure **3** ($n = 2$, $m = 1$) for the trimer agrees with the presence of extra OCH_3 peaks and a negligible tertiary H signal in the nmr spectrum (see Experimental Section). Similar oligomers are formed in the oxidative coupling of benzyl cyanides, α substituted with ester, acyl, or amide groups.[1]

The Cu/amine/O_2 oxidation system produced only low yields of dimer from **1a** and **1b**, owing to the prevalence of oxygenation over dehydrogenation; the glyoxylic esters **4a** and **4b**, isolated as 2,4-dinitrophenylhydrazones, were the main products. This is especially noteworthy, since the same oxidation system effected nearly quantitative dehydrogenation in the arylcyanoacetic esters series.[1]

The dimers **2** show the same type of radical dissociation–recombination equilibrium on heating (170–200°) as was found earlier with the arylcyanoacetic esters.[1] This was proven by the esr spectrum recorded by heating **2** in diphenyl ether–biphenyl at 202°. The spectrum was found to disappear again on cooling. The esr hyperfine coupling constants are in agreement with the structure of the radicals (Table II).[3] Moreover, dimers **2a** and **2b** were found to be active initiators for the free radical polymerization of styrene at 110°.[4]

Arylmalonodinitriles 5a–c.—Para-substituted arylmalonodinitriles **5b,c** were oxidatively coupled to the symmetrical dimers **6b** and **6c** with Mn(III) acetate in acetic acid and also electrochemically at a Pt anode in 90% acetic acid containing sodium acetate (controlled potential 450 mV/sce). The last two procedures were unsuccessful in producing C–C dimer from the unsubstituted dinitrile **5a**, because a substantial amount of benzylic C-para C oligomers was formed (with n up to 10), as was found with phenylmalonic ester **1a**. Under Hartzler's conditions [oxidation with $K_3Fe(CN)_6$, repeated by us with the same results], dimer **6a** apparently drops out of solution before oligomerization can take place.[5]

TABLE II

ESR HYPERFINE CONSTANTS (IN OERSTEDS) OF THE BENZYL RADICALS FROM THE DIMERS IN DIPHENYL ETHER/BIPHENYL

Radical precursor	Temp, °C	A(N)	$A(OCH_3)$	A_{ortho}	A_{meta}	A_{para}
2a	202		0.53	4.5	1.6	5.3
2b	202		0.5	4.4	1.5	5.8
6b[a]	83	1.89		4.03	1.23	5.9
8b	160	1.8	0.74	4.0	1.3	5.6
14a[a]	44	2.5	0.9[b]	1.4	1.5	2.7
14b[a]	60	2.5	0.84[b]	1.4	1.55	2.5

[a] In *m*-xylene. [b] OCH_2 (ester).

Dissociation of **6a** and **6b** into radicals occurs at 60°, as indicated by pink coloration, disappearing on cooling. The esr hyperfine splitting of **6b** (*m*-xylene solution at 83°) is consistent with the expected structure of the radicals (Table II).[3] It is noteworthy that Hartzler did not obtain esr spectra from **6a** and its di-*p*-NO_2 derivative. Apparently the lifetime of the radicals is too short in these cases.

Nmr spectra of **6b**, **8a**, and **13a** showed line broadening of all signals at temperatures >80°. McConnell[6] and Johnson[7] developed equations relating line width to rate constants for exchange reactions between diamagnetic and paramagnetic states. The contribution of such an exchange reaction to the width of a given nmr line is

$$\left(\frac{1}{T_2}\right)_{ex} = \frac{1}{\tau_d}\left[\left(\frac{a\tau_p}{2}\right)^2 \Big/ 1 + \left(\frac{a\tau_p}{2}\right)^2\right] \qquad (1)$$

In this equation τ_d and τ_t are the lifetimes of the diamagnetic and paramagnetic states, respectively, and a is the electron–nuclei coupling constant for the group of nuclei whose line width is being measured. In the case where $(a\tau_p/2)^2 \gg 1$, this equation reduces to

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[3] W. J. van den Hoek, W. G. B. Huysmans, and J. Smidt, unpublished work.

[4] H. A. P. de Jongh, C. R. H. I. de Jonge, W. G. B. Huysmans, H. J. M. Sinnige, W. J. de Klein, W. J. Mijs, and H. Jaspers, submitted for publication.

[5] H. D. Hartzler, *J. Org. Chem.*, **31**, 2654 (1966).

[6] H. M. McConnell and S. B. Berger, *J. Chem. Phys.*, **27**, 230 (1957).

[7] C. S. Johnson, *ibid.*, **39**, 2111 (1963). See also C. S. Johnson, *Advan. Magn. Resonance*, 33 (1965).

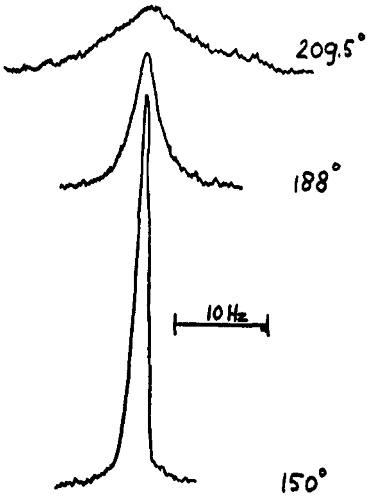


Figure 1.—Nmr spectra of diester **8a** (OCH_3 signal) at 150–210°.

$$\left(\frac{1}{T_2}\right)_{ex} = \frac{1}{\tau_d} \tag{2}$$

A sufficient condition to use eq 2 is that the esr spectrum of the paramagnetic species shows hyperfine interaction of the group of nuclei whose nmr line broadening is being measured. This condition was fulfilled for all protons of **6b**, **8a**, and **13a** (see Table III and Figure 1).

TABLE III

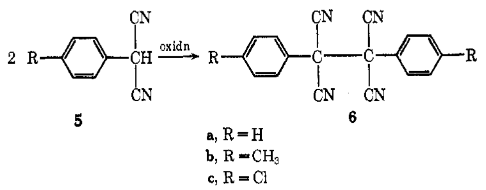
KINETIC PARAMETERS OF THE RADICAL DISSOCIATION REACTIONS, OBTAINED FROM NMR

Dimer	Temp range, °C	k_{diss} at 100°, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
6b	80–120	19.8	26	14
8a (dl)	170–210	0.001[a]	31	8
13a	80–120	14.4	14.5	−13

[a] By extrapolation.

From line width measurements of the methyl signal at different temperatures, k_{diss}, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were obtained in this way for the dissociation reaction of **6b**, **8a**, and **13a** (*cf.* Table III). $\Delta H^{\ddagger}$ is 5 kcal/mol lower than in the case of the racemic *p*-tolylcyanoacetic ester dimer **8a**, which reflects the greater radical stabilization by the CN groups.

Dimers **6b** and **6c** were found to be active free radical polymerization initiators for styrene at 70°.[3]



Methyl-Substituted Phenylcyanoacetic Esters 7 and 11.—Oxidative coupling of *p*-tolylcyanoacetic ester **7a** with O_2–$[Cu(OH)(TMEDA)]_2Cl_2$ in methanol gives dimer **8a** (mixture dl/meso 2:3) in 99% yield.[1]

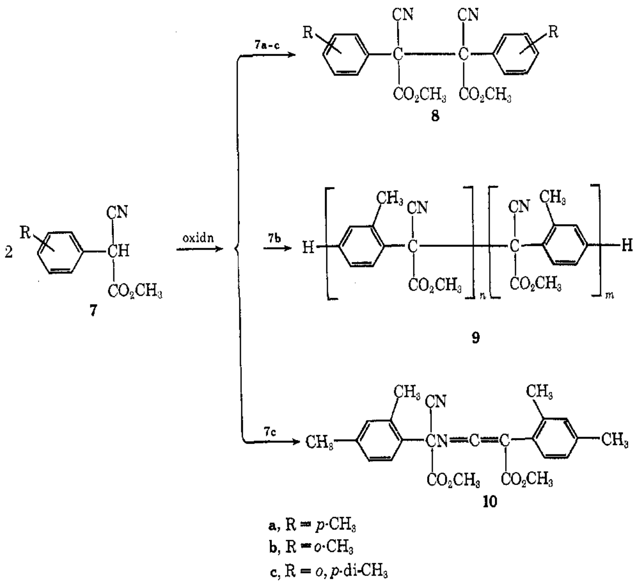
Under identical conditions, the *o*-tolylcyanoacetic ester **7b** consumed twice the amount of oxygen to give a complicated mixture. However, oxidation of **7b** with Ag_2O in benzene gave a 40% yield of C–C dimer **8b** (mixture dl/meso 3:2, determined by nmr;[1] see Experimental Section), together with oligomers. Gel permeation chromatography of the whole mixture showed the presence of about 55% of dimer **8b**, 35% of trimer, and 7% of tetramer. Apparently, the hindrance of the benzylic position by one *o*-CH_3 group promotes benzylic C–para C coupling to give oligomers **9**. The nmr spectrum shows no tertiary H. Oxidation of phenylcyanoacetic methyl ester itself (**7**, R = H) gives 2–4% of trimer as reported before.[1] According to the ir spectrum of the whole oxidation mixture (no C═C═N at 2010 cm^{-1}), no ketene imine similar to **10** could be detected.

As described earlier for **8a**, the kinetic mixture of **8b** (dl/meso 3:2) could be converted into a thermodynamic mixture (dl/meso 97:3 from nmr) by a 5-hr reflux in benzene.

Oxidation of *o,p*-dimethylphenylcyanoacetic ester **7c** with the O_2/Cu/amine system in methanol gave a 51% yield of dimer **8c** as one isomer. The dl configuration was assigned to this product on the basis of the nmr spectrum[1] (only *one* OCH_3 singlet at δ 3.88 ppm) and because a 5-hr reflux in benzene left dimer **8c** unchanged (compare dimer **8b**). The oligomerization of **7c** is impeded by the presence of a *p*-CH_3 group.

Oxidation of ester **7c** with Ag_2O in benzene gave a 1:1 mixture of dimer **8c** and ketene imine **10**, as indicated by ir and nmr spectra (see Experimental Section).

Diester **8c** dissociates reversibly into radicals, as shown by the esr spectrum (in diphenyl ether at 120–140°), which is too complex for interpretation in this case.



With **11a** and **11b**, however, the steric effect of the two *o*-CH_3 groups seems to inhibit oxidative coupling to the C–C dimer. Oxidation with Ag_2O in benzene now gives exclusively ketene imines **13a** and **13b** *via* C–N coupling. Stuart–Briegleb models show that formation of the usual C–C dimer is inhibited because of the steric effect of the *o*-CH_3 groups. Another example of radical C–N coupling to ketene imines by thermal decomposition of azobisnitriles has been reported by Hammond, *et al.*[8]

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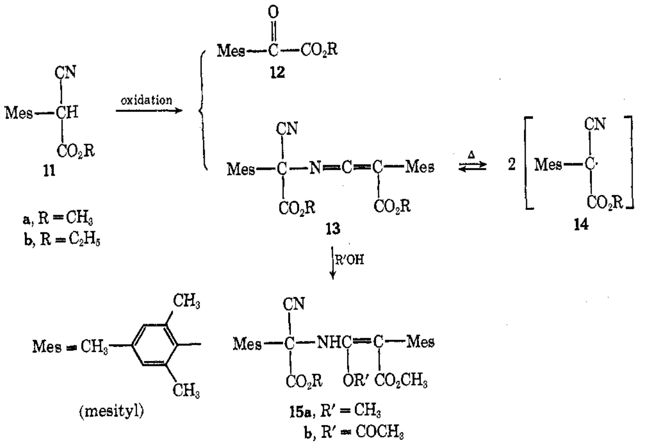
[8] C. S. Wu, G. S. Hammond, and J. M. Wright, *Amer. Chem. Soc.*, **82**, 5386 (1960); G. S. Hammond, C. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960).

Oxidation of **11a** with the O_2/Cu/amine system gave only a 9% yield of the ketene imine–methanol adduct **15a**, together with 50% of glyoxylic ester **12a**, (identified as the acid) owing to oxygenation. The methanol adduct **15a** was also formed from ketene imine **13a** by refluxing it in methanol.

Finally, when ester **11a** was oxidized with Mn(III) acetate in acetic acid in the presence of sodium acetate, both ketene imine **13a** and the acetic acid adduct **15b** were formed.



The facile dissociation of ketene imines **13a** and **13b** into radicals **14** is demonstrated by the development of a blue color on heating in solution. The blue color gradually deepens at 40–100° and disappears on cooling to room temperature. The esr hyperfine coupling constants (Table II) of the radicals **14** clearly indicate reduced spin density in the aromatic ring and enhanced spin density at the CN and the ester CH_3 groups[9] compared with the radical from **8a**. The o-CH_3 groups apparently reduce coplanarity of the $NC\text{–}\dot{C}\text{–}CO_2R$ moiety with the aromatic ring. The oxidative C–N coupling found with **11** is consistent with the enhanced spin density at the N atom, if we assume the same spin density distribution in the transition state of the coupling reaction.

Determination of k_{diss} from nmr line width measurements (as described in the previous section) of the ester CH_3 signal gave for **13** ⇄ **14** a relatively low $\Delta H^{\ddagger}$ (compared to **8a**) and a negative $\Delta S^{\ddagger}$ (*cf.* Table III). The lower $\Delta H^{\ddagger}$ is in agreement with the weaker C–N bond in the ketene imine **13a** compared to the C–C bond in **8a**.

The negative $\Delta S^{\ddagger}$, surprising at first sight for a dissociation reaction, might be accounted for by the greater freedom of motion in the ketene imine. Molecular models show that rotation of the $NC\text{–}\dot{C}\text{–}CO_2CH_3$ group is severely hindered in the radical **14**, whereas in the ketene imine **13**, the $\text{–N=C=C(Mes)}CO_2CH_3$ group just can rotate freely.

Experimental Section

Physical Methods and Analyses.—The melting points were determined with a melting point microscope (Leitz Model 553215) and are corrected; the boiling points are uncorrected. The ir spectra (KBr disks or neat) were recorded on a Hitachi EPI-G2 and a Perkin-Elmer 457 spectrophotometer. General features: the nitriles **5–15** showed a weak CN bond at 2250 cm^{-1} with varying intensities; the esters **1–4** and **7–15** gave a strong ester C=O band at 1750 cm^{-1}. Nmr spectra were run on an Varian A-60 spectrometer in $CDCl_3$ as solvent. Tetramethylsilane (δ 0) was used as an internal standard. Mass spectra were recorded at 70 eV with a Varian MAT CH-5 spectrometer. Gpc measurements were performed in THF solution on a gel permeation chromatograph, Model 200, manufactured by Waters Associates. The elemental analyses of new compounds were carried out under the supervision of Mr. W. J. Buis of the Micro-Analytical Department of the Institute for Organic Chemistry TNO (Utrecht, The Netherlands).

Esr Measurements.—Esr spectra were taken on a X-band spectrometer developed in our laboratory (Delft), using a TE_{011}-reflection cavity. The spectrometer was equipped with standard variable-temperature accessories. Temperatures were measured with a copper–constantan thermocouple outside the sample tube in the dewar just above the cavity.

Radicals were generated by heating a 0.01 *M* solution of the parent dimeric species under pure nitrogen (somewhat below 1 atm at 20°). The magnetic field was calibrated with Fremy's salt (A_N = 13.09 Oe). In all cases analysis of the spectra was confirmed by computer simulation.

Kinetic Measurements with Nmr Line Broadening.—Nmr line width measurements were recorded at a Jeol JNM-4H 100 MHz spectrometer equipped with a variable-temperature unit and a copper–constantan thermocouple inserted within the nmr tube for direct temperature reading. Temperature recording was accurate within ±0.5°; the temperature stability was better than 0.5°. Line width measurements were performed on the aromatic CH_3 and the ester OCH_3 signals, using α-chloronaphthalene as a solvent. For each of the dimers line width measurements were carried out at at least ten different temperatures relative to tetramethylthiourea, which was added to the solution. The line widths were independant of the dimer concentration.

Least square calculations yielded the Arrhenius activation parameters from the values of ln *k* and $1/T$. Variation coefficients were between 3 and 7%. The accuracy of the $\Delta S^{\ddagger}$ values was ±2 eu.

Arylmalonic Esters 1a–c.—Dimethyl phenylmalonate (**1a**) was prepared in 77% yield, mp 49.2–50.0°, after the method described by Nelson and Cretcher.[10] According to the same procedure there was obtained dimethyl *p*-tolylmalonate in 82% yield: mp 68.5–69.0°; nmr δ 2.28 (s, 3, *p*-CH_3), 3.67 (s, 6, OCH_3), 4.60 (s, 1, tertiary H), 7.0–7.4 (m, 4, aromatic H).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: C, 65.0; H, 6.5.

Dimethyl (*p*-chlorophenyl)malonate (**1c**) was obtained in 83% yield: mp 75.2–75.8°; nmr δ 3.67 (s, 6, OCH_3), 4.60 (s, 1, tertiary H), 7.0–7.4 (m, 4, aromatic H).

Anal. Calcd for $C_{11}H_{11}O_4Cl$: C, 54.43; H, 4.54; Cl, 14.64. Found: C, 54.6; H, 4.7; Cl, 14.5.

Arylmalonodinitriles 5a–c.—*p*-Tolylmalonodinitrile (**5b**) was prepared by heating *p*-tolylcyanoacetamide[1] with PCl_5 according to a procedure described for phenylmalonodinitrile (**5a**).[11] After crystallization from ethanol there was obtained 40% of **5b**: mp 57–57.5°; nmr (CCl_4) δ 2.40 (s, 3, *p*-CH_3), 5.08 (s, 1, tertiary H), 7.4 (AB system, 4 aromatic H).

Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 77.0; H, 5.3; N, 17.9.

p-Chlorophenylmalonodinitrile (**5c**) was prepared from *p*-chlorophenylcyanoacetamide as described for **5b**: mp 70.2–70.7°; nmr δ 5.16 (s, 1, tertiary H), 7.60 (s, 4, aromatic H). The *p*-chlorophenylcyanoacetamide was synthesized from methyl *p*-chlorophenylcyanoacetate and ammonia as described for phenylcyanoacetamide,[12] yield 84%, mp 122–124° after one crystallization from ethanol.

Anal. Calcd for $C_9H_5N_2Cl$: C, 61.21; H, 2.85; N, 15.87; Cl, 20.08. Found: C, 60.9; H, 3.0; N, 15.7; Cl, 20.2.

Arylcyanoacetic Esters 7b, 7c, 11a, and 11b.—Methyl *o*-tolylcyanoacetate (**7b**) was prepared in 64% yield from *o*-methylbenzyl cyanide, bp 118–128° (12 mm), and dimethyl carbonate (3 molar excess) with CH_3ONa in refluxing toluene as described for ethyl phenylcyanoacetate:[13] bp 106–114° (0.3 mm); nmr

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[9] A theoretical treatment of the esr data will be given elsewhere by W. J. van den Hoek and J. Smidt, Technische Hogeschool, Delft.

[10] W. L. Nelson and L. H. Cretcher, *J. Amer. Chem. Soc.*, **50**, 2760 (1928).

[11] J. C. Hessler, *Amer. Chem. J.*, **32**, 123 (1904).

[12] B. Radziszewski and P. Wispek, *Chem. Ber.*, **18**, 1279 (1885).

[13] N. Rabjohn, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 461.

δ 2.32 (s, 3, *o*-CH$_3$), 3.67 (s, 3, OCH$_3$), 4.83 (s, 1, tertiary H), 7.0–7.5 (m, 4, aromatic H).

Methyl 2,4-dimethylphenylcyanoacetate (**7c**) was prepared in 71% yield from 2,4-dimethylbenzyl cyanide[14] and dimethyl carbonate as described for **7b**, bp 114–120° (0.7 mm). Two crystallizations from methanol–water gave a pure sample: mp 71.3–74.5°; nmr δ 2.30 (s, 3, aromatic CH$_3$), 2.33 (s, 3, aromatic CH$_3$), 3.77 (s, 3, OCH$_3$), 4.87 (s, 1, tertiary H), and 7.0–7.5 (m, 3, aromatic H).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.9; H, 6.5; N, 6.9.

Methyl 2,4,6-trimethylphenylcyanoacetate (**11a**) was prepared from 2,4,6-trimethylbenzyl cyanide[14] and dimethyl carbonate with NaH in dimethoxyethane as described for methyl phenylcyanoacetate.[1] The crude product was not distilled but was immediately recrystallized from ether–cyclohexane (1:9), giving a 21% yield of colorless material, mp 99.6–101.8°. One more recrystallization gave pure ester **11a**: mp 102.3–102.6°; nmr δ 2.28 (s, 3, *p*-CH$_3$), 2.37 (s, 6, *o*-CH$_3$), 3.78 (s, 3, OCH$_3$), 5.18 (s, 1, tertiary H), and 6.95 (s, 2, *m*-H).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.0; H, 7.0; N, 6.4.

Ethyl 2,4,6-trimethylphenylcyanoacetate (**11b**) was prepared from 2,4,6-trimethylphenylbenzyl cyanide[13] and diethyl carbonate with C_2H_5ONa in refluxing toluene as described for ethyl phenylcyanoacetate.[1] There was obtained a 41% yield of crystalline product: bp 124–126° (0.4 mm); mp 61–66°; nmr δ 1.23 (t, 3, ethyl CH$_3$, $J = 7.0$ cps), 2.22 (s, 3, *p*-CH$_3$), 2.33 (s, 6, *o*-CH$_3$), 4.20 (q, 2 ,CH$_2$, $J = 7.0$ cps); 5.08 (s, 1, tertiary H), and 6.83 (s, 2, *m*-H).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 73.0; H, 7.5; N, 6.0.

Tetraesters 2a–c. Oxidative Coupling of 1b with KMnO$_4$ in Acetone–Ammonia.—Dimethyl *p*-tolylmalonate (**1b**, 4.44 g, 20 mmol) was dissolved in a mixture of 160 ml of acetone and 40 ml of concentrated ammonia. KMnO$_4$ (3.6 g, 23 mmol) was added in small portions over a period of 5 min. The reaction mixture was kept at 20–30° and was stirred magnetically. After 30 min the reaction mixture was acidified with 4 *N* HCl. Extraction with chloroform yielded, after washing three times with 50 ml of water, drying over MgSO$_4$, filtration, and evaporation *in vacuo*, a slightly yellow sirup (4.3 g). Crystallization from methanol afforded 3.5 g (80%) of colorless dimer **2b**: mp 161.1–161.7° (*Anal.* Calcd: C, 65.16; H, 5.88. Found: C, 64.7; H, 6.0.), nmr δ 2.27 (s, 6, aromatic CH$_3$), 3.77 (s, 12, OCH$_3$), and 6.8–7.0 (m, 8, aromatic H).

Oxidative Coupling of 1b with K$_3$Fe(CN)$_6$ in Methanol–Ammonia.—To a solution of 4.44 g (20 mmol) of dimethyl *p*-tolylmalonate (**1b**) in 80 ml of methanol was slowly added a solution of 6.8 g (21 mmol) of $K_3Fe(CN)_6$ in 60 ml of concentrated ammonia, while stirring at room temperature. After 30 min there was added 100 ml of water and the mixture was extracted with chloroform. After the usual work-up (see previous experiment) there was obtained 3.6 g (81%) of colorless dimer **2b**.

Oxidative Coupling of 1b with O$_2$/Cu/Amine in Methanol.—The oxidation was carried out in a 250-ml oblong flask with 11.1 g (50 mmol) of dimethyl *p*-tolylmalonate (**1b**) in 110 ml of methanol at 20° with oxygen using 1.25 g (2.5 mmol) of CuCl-TMEDA as catalyst. The oxygen uptake was followed by means of a gas buret. After 2 hr, 850 ml of oxygen was consumed (calcd 300 ml for an oxidative C–C coupling to give **2b**). The reaction mixture was acidified with 5 ml of 2 *N* HCl and extracted with chloroform. After the usual work-up (see before) there was obtained 11.0 g of a liquid. Crystallization from methanol gave 1.4 g (13%) of dimer **2b**. Treatment of the mother liquor with 2,4-dinitrophenylhydrazine in methanol–sulfuric acid yielded 11.8 g (53%) of the 2,4-dinitrophenylhydrazone of the glyoxylic ester **4b**, mp 168.8–169.2°.

Oxidative Coupling of 1a with KMnO$_4$ in Acetone–Ammonia.—Dimethyl phenylmalonate (**1a**, 4.2 g, 20 mmol) was oxidized according to the procedure described above. After crystallization of the crude product (4.1 g) from methanol there was obtained 0.4 g (10%) of dimer **2a**, mp 191.0–192.5° (reported[2] mp 192°). (*Anal.* Calcd: C, 63.77; H, 5.31. Found: C, 63.7; H, 5.3.); nmr δ 3.80 (s, 12, OCH$_3$) and 6.8–7.3 (m, 10, aromatic H). Gpc measurements of the mother liquor showed the presence of *ca.* 40% dimer, 40% trimer, and 10% tetramer (shoulder).

Chromatography of the whole oxidation product over silica gel (0.05–0.2 mm) using 3% acetone in CCl$_4$ as eluent gave besides dimer **2a** also noncrystalline fractions with additional nmr peaks: δ 3.67, 3.73, and 3.77 (s, OCH$_3$), 4.58 (s, 1.7% of total OCH$_3$ peaks, tertiary H).

Oxidative Coupling of 1a with K$_3$Fe(CN)$_6$ in Aqueous NaOH/CH$_2$Cl$_2$.—To a mixture of 4.2 g (20 mmol) of dimethyl phenylmalonate (**1a**) dissolved in 50 ml of methylene chloride and 20 ml of 2 *N* NaOH there was added 20 ml of a 1 *N* $K_3Fe(CN)_6$ solution in water and after shaking for 20 min in a separatory funnel the layers were separated. The water layer was extracted three times with 10 ml of methylene chloride. The combined methylene chloride solutions were washed with water and dried over MgSO$_4$.

Evaporation *in vacuo* of methylene chloride and crystallization from methanol gave 0.45 g (11%) of dimer **2a**.

Oxidative Coupling of 1a with O$_2$/Cu/Amine in Methanol.—Dimethyl phenylmalonate (**1a**, 4.2 g, 20 mmol) was oxidized after the procedure described above. Crystallization from methanol yielded 0.14 g (3.4%) of dimer **2a**. Treatment of the mother liquor with 2,4-dinitrophenylhydrazine in methanol–sulfuric acid gave 2.9 g (42%) of the 2,4-dinitrophenylhydrazone of the glyoxylic ester **4a**, mp 172.2–172.7° (reported[15] mp 173–174°).

Oxidative Coupling of 1c with KMnO$_4$ in Acetone–Ammonia.—Dimethyl (*p*-chlorophenyl)malonate (**1c**, 4.84 g, 20 mmol) was oxidized after the method described above. Crystallization from methanol afforded 3.3 g (68%) of colorless dimer **2c**: mp 167.5–169.5° (*Anal.* Calcd: C, 54.66; H, 4.14; Cl, 14.70. Found: C, 54.6; H, 4.3; Cl, 14.6.); nmr δ 3.82 (s, 12, OCH$_3$) and 6.8–7.3 (m, 8, aromatic H).

Oxidative Coupling of 1c with K$_3$Fe(CN)$_6$ in Methanol-Ammonia.—Dimethyl (*p*-chlorophenyl)malonate (**1c**, 4.84 g, 20 mmol) was oxidized after the procedure described above. Crystallization from methanol gave 3.8 g (78%) of dimer **2c**.

Tetranitriles 6b and 6c. Oxidative Coupling of 5b with Mn(III) Acetate.—To a solution of 7.8 g (0.050 mmol) of *p*-tolylmalonodinitrile (**5b**) in 50 ml of acetic acid was added a solution of 11 g (0.048 mmol) of Mn(III) acetate in 100 ml of 98% acetic acid containing 10 g of sodium acetate. The sodium acetate was added to facilitate the dissolution of Mn(III) acetate. The reaction product precipitated, and was filtered and washed with water. Crystallization from toluene gave a 95% yield of tetranitrile **6b**: mp 201–202°; nmr (acetone-*d*$_6$) δ 2.50 (s, 6, CH$_3$), 7.51 (AB spectrum, 8, aromatic H); mass spectrum *m/e* 310 (molecular ion), 155 [*p*-tolyl-C(CN)$_2$].

Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05; mol wt, 310. Found: C, 77.4; H, 4.7; N, 17.8.

Oxidative Coupling of 5c with Mn(III) Acetate.—The oxidation was carried out as described for **5b** and gave a 93% yield of tetranitrile **6c**, mp 215°, nmr δ 7.60 (s, aromatic H).

Electrochemical Coupling of 5b.—A solution of 100 mg (0.64 mmol) of *p*-tolylmalodinitrile (**5b**) and 0.03 mmol of sodium acetate in 60 ml of 90% acetic acid–water was electrolyzed in a thermostatted cell at 31° at a controlled potential of 450 mV (sce) at a Pt anode. After electrolysis the solution was concentrated to 20 ml and the product was precipitated by the addition of water. The precipitate was filtered, washed with water, and dried to give a 80% yield of dimer **6b** (current yield 85%).

Oxidation of Methyl-Substituted Phenylcyanoacetic Esters 7b and 7c and 11a and 11b. Oxidation of 7b with Ag$_2$O.—A solution of 9.45 g (0.05 mmol) of methyl *o*-tolylcyanoacetate (**7b**) in 100 ml of benzene containing 6.0 g (0.026 mmol) of Ag$_2$O was stirred for 30 min at room temperature. After filtration the benzene was removed *in vacuo*. Chromatography of the residue over 600 g of silica gel (0.05–0.2 mm) gave after elution with 3% ethyl acetate in CCl$_4$ 3.8 g of colorless dimer **8b**. On heating at a rate of 10°/min the dimer (isomer mixture) melted partially at 153°, then it recrystallized completely (conversion to dl isomer): mp 177.4–180.8°; nmr δ 1.81 and 1.98 (s, 6, *o*-CH$_3$, ratio 3:2, dl and meso isomer), 3.86 and 3.95 (s, 6, OCH$_3$, ratio 2:3, meso and dl isomer), 7.0–7.5 (m, 8, aromatic H).

Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.21; H, 5.32; N, 7.45. Found: C, 70.2; H, 5.4; N, 7.4.

Attempts to obtain pure meso isomer by fractional crystallization as described for **7a**[1] failed.

Gpc analysis of the whole reaction mixture corresponded with the presence of *ca.* 55% dimer, 35% trimer, and 7% tetramer.

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[14] B. van Zanten and W. T. Nauta, *Recl. Trav. Chim. Pays-Bas*, **79**, 1215 (1960).

[15] P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Amer. Chem. Soc.*, **82**, 6136 (1960).

Nmr of reaction mixture was the same as that of **8b**, except for additional peaks at δ 2.14 and 2.31 (s, *o*-CH_3) and 3.90 (s, OCH_3) and *no* peak at δ 4.83 (tertiary H).

Thermal Equilibration of 8b to Give Racemic Isomer.—A solution of 500 mg of dimer **8b** (dl/meso 3:2) in 20 ml of benzene was refluxed for 1 hr. There was obtained a 93:7 mixture of dl/meso (by nmr). Recrystallization from methanol gave pure dl isomer: mp 180–183°; yield 70%; nmr δ 1.81 (s, 6, *o*-CH_3), 3.95 (s, 6, OCH_3), 7.0–7.4 (m, 8, aromatic H).

Diester 8c by Oxidative Coupling of 7c with Cu/Amine/O_2.—A solution of 160 g (0.79 mol) of ester **7c**, bp 114–120° (0.7 mm), and 5.0 g (11 mmol) of $[Cu(OH)TMDA]_2Cl_2$ in 160 ml of methanol was shaken with oxygen at room temperature in an oblong flask connected with a gas buret. After consumption of the theoretical amount of oxygen (0.2 g-atom in 7.5 min), there was added 1 l. of 0.1 *N* hydrochloric acid and the mixture was extracted two times with $CHCl_3$. The combined chloroform layers were washed with water and dried over molecular sieves. Evaporation of the filtrate *in vacuo* gave a yellow sirup. Addition of about 80 ml of methanol gave immediate crystallization and a first crop of 60 g of colorless, pure diester **8c**, mp 198.4–199°, was obtained. Addition of water to the mother liquor gave 35 g of yellow product, which on recrystallization from methanol gave another 22 g of pure diester **8c**: mp 195.2–197°; total yield 51%; nmr δ 1.77 (s, 6, *o*-CH_3), 2.27 (s, 6, *p*-CH_3), 3.88 (s, 6, OCH_3, dl isomer[1]), 6.8–7.2 (s, 6, aromatic H); mass spectrum *m/e* 404 (molecular ion), 202 (base peak, rupture of central C–C bond).

Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found: C, 71.0; H, 6.0; N, 6.8.

Thermal Treatment of Diester 8c.—Under conditions in which diester **8a** is equilibrated into 94% dl isomer[1] and diester **8b** into 97% dl isomer (a 5-hr reflux in benzene), diester **8c** is recovered unchanged. Therefore, the dl configuration is assigned to diester **8c**. The presence of a second isomer has never been detected.

Diester 8c and Ketene Imine 10 by Oxidative Coupling of 7c with Ag_2O.—A solution of 2.0 g (10 mmol) of ester **1c** in 100 ml of benzene containing 1.4 g (6 mmol) of Ag_2O was stirred at room temperature for 2 hr. Evaporation of the filtrate *in vacuo* gave 2.0 g of a glassy residue: ir (KBr) 2250 (w, CN), 2025 (m, C=C=N), 1750 (vs, unconjugated C=O), 1720 cm^{-1} (m, conjugated C=O); nmr, same as that of **8c**, except for extra peaks at δ 1.97 (s, *o*-CH_3 of ketene imine moiety) and 3.83 (s, OCH_3 of ketene imine moiety), corresponding to a 1:1 mixture of dimer **8c** and ketene imine **10**.

Crystallization from ligroin (bp 60–80°) gave a first crop of 0.28 g of colorless diester **8c**, mp 193.7–196.5. Upon standing overnight, the mother liquor furnished another 0.80 g of diester **8c**, mp 190–197° (total yield 54%). The ir and nmr spectra of both fractions are identical with those of diester **8c**, prepared before.

Ketene Imine 13a by Oxidative Coupling of 11a with Ag_2O.—A solution of 2.17 g (10 mmol) of ester **11a**, 95–100°, in 75 ml of benzene containing 1.4 g (6 mmol) of Ag_2O was stirred at room temperature for 3 hr. Evaporation of the filtrate gave 2.10 g (97%) of colorless sirup, which was practically pure ketene imine **13** by ir, nmr, and tlc (eluent: benzene–ethyl acetate, 9:1). The sirup was dissolved in boiling ligroin. After intensive scratching at room temperature a very slow crystallization started, and after 2 hr at 0° a first crop was obtained of 0.38 g of colorless ketene imine **13**, mp 116.8–117.3°. Upon standing overnight, the mother liquor furnished another 0.65 g of colorless product: mp 117.5–119.6°; ir 2250 (vw, CN), 2010 (s, C=C=N), 1763 (s, saturated C=O), 1718 (m, C=C–C=O), 1700 cm^{-1} (s, C=C–C=O); nmr δ 2.18, 2.24, and 2.35 (s, 3 × 6, *o*- and *p*-CH_3), 3.71 and 3.82 (s, 2 × 3, OCH_3), 6.83 (s, 4, aromatic H); mass spectrum *m/e* 432 (molecular ion), 216 (strong, rupture of central C–N bond).

Anal. Calcd for $C_{26}H_{28}N_2O_4$: C, 72.20; H, 6.52; N, 6.48; mol wt, 432.5. Found: C, 72.1; H, 6.6; N, 6.6.

Oxidation of Ester 11a with Cu/Amine/O_2 to Give 12a and 15a.—A solution of 4.34 g (20 mmol) of ester **11a**, mp 98–101°, and 0.5 g (1.1 mmol) of $[Cu(OH)TMEDA]_2Cl_2$ in 50 ml of methanol was shaken at room temperature with oxygen as described for diester **8c**. After 30 min there was consumed 60 ml (2.5 g-atoms), after 6 hr 220 ml (9 g-atoms) of oxygen. Addition of 500 ml of 0.1 *N* hydrochloric acid followed by chloroform extraction (see diester **8c**) gave 4.7 g of a yellow oil. Chromatography over silica gel (0.05–0.2 mm) with 3% EtOAc in CCl_4 as eluent gave 2.1 g (50%) of a yellow oil, corresponding to methyl 2,4,6-trimethylphenylglyoxylate (**12a**): ir (neat) 1780, 1760, 1740, and 1705 cm^{-1} (C=O); nmr 2.25 (s, 6, *o*-CH_3), 2.29 (s, 3, *p*-CH_3), 3.90 (s, 3, OCH_3), 6.93 (s, 2, *m*-H); mass spectrum *m/e* 206 (molecular ion, very weak), 147 (base peak, Mes-CO), 119 (80% of base peak, Mes).

Hydrolysis of ester **12a** with NaOH in aqueous ethanol (1 hr reflux) gave mesitylglyoxylic acid, which after two recrystallizations from benzene–hexane melted at 115.5–118.5° dec (reported[16] mp 116.7–117.9°).

Further elution gave 0.40 g (9%) of colorless enol ether **15a**: mp 165.8–166.3°; ir 3450 (broad, NH), 3210 and 3150 (m, NH), 2250 (vw, CN), 1775 and 1670 (s, CO), 1620 (sh) and 1595 cm^{-1} (s) (C=C); nmr δ 2.06 (s, 3, aromatic CH_3), 2.21 (s, 3, aromatic CH_3), 2.25 (s, 6, aromatic CH_3), 2.57 (s, 6, aromatic CH_3), 2.87 (s, 3, C=$COCH_3$), 3.62 (s, 3, ester OCH_3), 3.93 (s, 3, ester OCH_3), 6.92 (s, 4, *m*-H); mass spectrum *m/e* 464 (molecular ion).

Anal. Calcd for $C_{27}H_{32}N_2O_5$: C, 69.80; H, 6.94; N, 6.03; mol wt, 464.6. Found: C, 69.8; H, 7.0; N, 5.9.

Methanol Adduct 15a from Ketene Imine 13a.—A solution of 500 mg (1.2 mmol) of ketene imine **13a** in 25 ml of methanol was refluxed until the blue color had disappeared (3 hr).

The solution was concentrated to 10 ml and water was added to the hot solution until a slight turbidity persisted. Upon standing at room temperature, a first crop of 180 mg of product, mp 106–111°, was obtained. From the mother liquor there was obtained a second crop of 230 mg of crystals, mp 98–99.6°, identical with methyl mesitylcyanoacetate (**11a**).

An ether solution of the first crop was shaken with 1 *N* NaOH solution to remove **11a** and the ether layer was dried ($MgSO_4$) and evaporated. Two recrystallizations of the residue from methanol gave the methanol adduct **15a**, mp 160–166°. The ir and nmr spectra are identical with those of **15a**, prepared before.

Oxidation of 11a with Mn(III) Acetate to Give 13a and 15b.—A solution of 1.87 g (8.2 mmol) of Mn(III) acetate and 4.08 g of $NaOAc \cdot 3H_2O$ in 100 ml of acetic acid was slowly added to a solution of 1.02 g (4.7 mmol) of methyl mesitylcyanoacetate (**11a**) and 4.08 g of $NaOAc \cdot 3H_2O$ in 30 ml of acetic acid at 80°. After 10 min the reaction was stopped. After removal of about 70 ml of acetic acid *in vacuo*, the resulting solution was divided into two equal parts.

One part was evaporated to dryness *in vacuo*. The residue was extracted with chloroform and the solvent was slowly evaporated until crystallization just started. There was obtained 100 mg (20%) of a colorless product, mp 118.5–119.2°, the ir and nmr spectra of which are identical with those of ketene imine **13a**, prepared before.

To the second part, water was added until the solution became slightly turbid. After 2 days at 5°, 300 mg (50%) of acetic acid adduct **15b**, mp 164.5–165.2°, was isolated: ir 3450 (broad, NH), 3240 and 3190 (m, NH), 1798 and 1772 (s, CO), 1685 and 1608 cm^{-1} (s, C=C); nmr δ 1.25 (s, 3, $COCH_3$), 2.02 (s, 3, aromatic CH_3), 2.22 (s, 9, aromatic CH_3), 2.53 (s, 6, aromatic CH_3), 3.66 (s, 3, OCH_3), 3.94 (s, 3, OCH_3), 6.87 (s, 4, *m*-H); mass spectrum *m/e* 492 (molecular ion).

Ketene Imine 13b by Oxidation of 11b with Ag_2O.—A solution of 2.3 g (10 mmol) of ester **11b**, mp 61–66°, in 75 ml of benzene containing 1.5 g (6.5 mmol) of Ag_2O was stirred overnight at room temperature. The colorless sirup, obtained on evaporation of the filtrate, was recrystallized from hexane. A first crop of 0.95 g of **13b**, mp 90.1–91.7°, was obtained. Concentration of the mother liquor gave another 0.28 g of product: mp 90–92°; total yield 54%; ir 2230 (vw, CN), 2020 (s, C=C=N), 1770 and 1760 (s, saturated CO), 1722 and 1718 cm^{-1} (s, C=C–C=O); nmr δ 1.18 (t, J = 7.0 cps, 3, ethyl CH_3), 1.23 (t, J = 7.0 cps, 3, ethyl CH_3), 2.20 (s, 12, aromatic CH_3), 2.38 (s, 6, aromatic CH_3), 4.19 (q, J = 7.0 cps, 2, CH_2), 4.23 (q, J = 7.0 cps, 2, CH_2), 6.98 (s, 4, *m*-H); mass spectrum *m/e* 460 (molecular ion), 230 (base peak, rupture of central C–N bond).

Anal. Calcd for $C_{28}H_{32}N_2O_4$: C, 73.02; H, 7.00; N, 6.08; mol wt, 460.6. Found: C, 72.8; H, 7.1; N, 6.1.

Registry No.—**1b**, 34402-91-0; **1c**, 34402-92-1; **2a**, 34404-71-2; **2b**, 34404-72-3; **2c**, 34404-73-4; **4b** 2,4-DNP, 34404-74-5; **5b**, 33534-88-2; **5c**, 32122-64-8;

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(16) W. G. Dauben and J. B. Rogan, *J. Amer. Chem. Soc.*, **78**, 4135 (1956).

6b, 34404-77-8; **6c**, 34404-78-9; **7b**, 34404-79-0; **7c**, 34404-80-3; *dl*-**8a**, 30698-38-5; *dl*-**8b**, 34405-36-2; *dl*-**8c**, 34405-37-3; **11a**, 34404-81-4; **11b**, 34404-82-5; **12a**, 34404-83-6; **13a**, 34404-84-7; **13b**, 34404-85-8; **14a**, 34415-49-1; **14b**, 34415-50-4; **15a**, 34404-86-9; **15b**, 34404-87-0.

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Reactions of α-Substituted Polynitrotoluenes. III. 2,4,6-Trinitrobenzyl Anion as a Nucleophile at Aromatic Carbon

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The results of deuterium exchange experiments have shown that 2,4,6-trinitrobenzyl anion is formed from 2,4,6-trinitrotoluene in alkaline tetrahydrofuran–methanol solutions. This carbanion has been utilized as a nucleophile in halogen displacement reactions at aromatic carbon to prepare a series of polynitrodiphenylmethanes.

The previous paper in this series[1] described the preparation of 2,2′,4,4′,6,6′-hexanitrostilbene (**1**) from 2,4,6-trinitrotoluene (**2**) and aqueous hypochlorite in tetrahydrofuran–methanol. It was postulated[1] that, in alkaline media, **2** formed 2,4,6-trinitrobenzyl anion (**3**), which was chlorinated to yield 2,4,6-trinitrobenzyl chloride (**4**). Subsequent reaction of **4** with alkali produced **1**. Evidence to support the intermediacy of **4** in this reaction was obtained by isolating it in 85% yield from a short-stopped reaction.

In the present paper, we present additional evidence for the existence of the anion **3** under our reaction conditions and describe a variety of chemistry based upon its use as a nucleophile in displacement reactions at aromatic carbon. The products of these reactions, polynitrodiphenylmethanes, dissociate in alkaline media to form the corresponding polynitrodiphenylmethide ions. These anions were found to be unreactive in nucleophilic addition reactions.

Results and Discussion

The question of the existence of the anion **3** has been considered by numerous investigators.[2-7] In general, the formation of the anion **3** was disfavored in largely aqueous solvent systems. This conclusion was recently confirmed by Bernasconi,[8] who observed that though the anion **3** is the primary product of the reaction of **2** with alkali in methanol, ethanol, and 50% dioxane–water, there was no evidence to suggest that the anion **3** was present when 10% dioxane–water was used as a solvent.

Since our experimental work[1] had been carried out in tetrahydrofuran–methanol–water, about 1:1:1, our preliminary experiments were designed to determine whether **3** is in fact the primary product formed from **2** upon the addition of alkali. If the anion **3** does form, then in a reaction such as the halogenation of **2**,[1] the formation of **3** should be rate determining.[9a] If halogenation of **3** is rapid relative to its rate of reprotonation by the weak acids water or methanol, then every anion formed will be converted to **4** without returning to **2**. Thus, the conversion of **2** to **4** in a deuterated solvent system should yield **4**-α-H_2.

When **2** in tetrahydrofuran–methanol-*d* was rapidly added to D_2O–OD^- at 0° and the mixture was immediately quenched in DCl–D_2O, the recovered **2** was found to have exchanged 12.4% (nmr) of its methyl protons. Quenching the reaction after a 30-sec equilibration increased the deuterium content of the recovered **2** to 25.5%. However, when the anion **3** was trapped by chlorination[1] in a deuterated solvent system, the halide **4** did not contain any deuterium in the α position. These results are consistent with the proposed slow formation of **3** from **2** (eq 1) followed by a rapid chlorination of the anion **3**.

$$\underset{\mathbf{2}}{\mathrm{PiCH_3}} + \mathrm{OH^-} \longrightarrow \underset{\mathbf{3}}{\mathrm{PiCH_2^-}} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{PiCH_2^-} + \mathrm{OCl^-} + \mathrm{H_2O} \longrightarrow \underset{\mathbf{4}}{\mathrm{PiCH_2Cl}} + 2\mathrm{OH^-} \qquad (2)$$

Pi = 2,4,6-trinitrophenyl

A similar and perhaps rather surprising result was obtained when *p*-nitrobenzyl bromide was used as the substrate molecule for nucleophilic attack by the anion **3**.[1] From this reaction carried out in tetrahydrofuran–methanol-*d*, we obtained an 83% yield of 2,4,4′,6-tetranitrobibenzyl (**5**). The product had not incorporated deuterium at either of the methylene groups (eq 3). The absence of deuterium in the product suggests that the nucleophilic displacement process involving either ionic or ion–radical[9b] intermediates is exceedingly rapid as compared to the recombination of

$$\mathrm{PiCH_2^-} + p\text{-}\mathrm{O_2NC_6H_4CH_2Br} \longrightarrow \underset{\mathbf{5}}{p\text{-}\mathrm{O_2NC_6H_4CH_2CH_2Pi}} \qquad (3)$$

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[1] K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966).

[2] K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).

[3] E. Buncell, K. E. Russell, and J. Wood, *Chem. Commun.*, 252 (1968).

[4] R. E. Miller and W. F. R. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).

[5] J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).

[6] E. F. Caldin and G. Long, *Proc. Roy. Soc., Ser. A*, **228**, 263 (1955).

[7] K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

[8] C. F. Bernasconi, *J. Org. Chem.*, **36**, 1671 (1971).

[9] (a) By analogy with the overall rate of halogenation of other carbon acids: R. G. Pearson and R. L. Dillion, *J. Amer. Chem. Soc.*, **75**, 2439 (1953). Bernasconi[8] reports that the deprotonation of **2** in methanol or ethanol is as slow as in nitroethane. (b) R. G. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, **87**, 4520 (1965).