components) and the small amount of unchanged chloride (estimated from comparing areas of the chloride peak and the peak due to cyclohexane and C_7 components in a chromatogram with column C) from the weight of the crude product. Methylcyclohexane and bicyclo[4.1.0]heptane were identified by comparison of their infrared spectra with those of authentic samples. Methylenecyclohexane was identified by a comparison of the infrared spectrum of the gas with that reported for a liquid sample.[12] A reaction run in the same manner using *n*-tetradecane as solvent gave very similar results.

Reaction of Cyclopentylmethyl Chloride with Sodium.—In a similar manner, 5.0 g. of chloride was added over 75 min. to 1.4 g. of sodium in 4 ml. of isooctane, and the reaction mixture then was heated gradually to 100° over 1 hr. The yield of C_6 hydrocarbons was calculated by correcting the weight of the crude product by the same procedure described for the reaction with cyclohexylmethyl chloride. Chromatography of the reaction mixture over column D gave, in order of elution, methylcyclopentane, methylenecyclopentane, and a mixture of bicyclo[3.1.0]hexane and cyclohexene. Methylcyclopentane was identified by comparison of its infrared spectrum with API 14,[13] and methylenecyclopentane by comparison of the spectrum of the gas with that reported for a liquid sample[14]; cyclohexane has the same retention time but the infrared spectrum indicates that it could not be present in significant amount. Bicyclo[3.1.0]hexane was identified by the n.m.r. spectrum of a carbon tetrachloride solution which had complex absorption from τ 8.2 to 9.0.[15] Cyclohexene has the same retention time as bicyclo[3.1.0]hexane, and its presence was detected and its amount was estimated by the presence of weak absorption at τ 4.4 (identical in position with the absorption of authentic cyclohexene). A reaction run in the same manner in *n*-tetradecane gave similar results.

Reaction of Cyclobutylmethyl Chloride with Sodium.—In a similar manner, 2.1 g. of cyclobutylmethyl chloride was added over 1 hr. to 1.1 g. of sodium in 1.4 ml. of *n*-tetradecane. Chromatography of the reaction mixture over column D gave, in order of elution, 1-pentene, methylcyclobutane, methylenecyclobutane, cyclopentene, and bicyclo[2.1.0]pentane. Cyclopentene and 1-pentene were identified by comparison of their infrared spectra with those of authentic samples. Methylcyclobutane and methylenecyclobutane were identified by comparison of their spectra with API 890 and 561, respectively.[13] Bicyclo[2.1.0]pentane was identified by the close comparison of the infrared spectrum of a carbon tetrachloride solution with that reported for the pure liquid[16] and also by comparison of its n.m.r. spectrum with one reported.[17] Cyclopentane has the same retention time as methylenecyclobutane but was shown to be absent by examination of the n.m.r. spectrum. In a similar reaction with chloride containing 15% of cyclopentyl chloride, cyclopentane (identified by comparison of its infrared spectrum with API 446)[13] was shown to comprise 14% of the product by rechromatographing the "methylenecyclobutane" fraction over column B which eluted cyclopentane before methylenecyclobutane. A reaction with 1.2 g. of cyclopentyl chloride and 4.0 g. of cyclohexylmethyl chloride led to cyclopentane (32%) and cyclopentene (68%) as the only detected C_5 products.

Reactions of Cyclopropylmethyl Chloride with Phenylsodium and Sodium.—Phenylsodium was prepared in 12 ml. of isooctane from 7.5 g. (0.067 mole) of chlorobenzene and a dispersion of 2.2 g. (0.096 g.-atom) of sodium in 4.2 g. of mineral oil. Then a solution of 1.99 g. (0.022 mole) of cyclopropylmethyl chloride in 5 ml. of isooctane was added over 45 min. Nitrogen was passed continually over the reaction mixture, and the exit gases were passed through a trap cooled in liquid nitrogen. The reaction mixture was stirred for an additional 90 min. Then the material in the trap was transferred to a vacuum line and was fractionated crudely by two distillations through a Dry Ice trap to remove less volatile components. Chromatography over column D gave, in order of elution, ethylene, 1-butene, butadiene, cyclobutene, and an unidentified peak. Ethylene was identified by its retention time. Butadiene and 1-butene were identified by comparison of their infrared spectra with API 917 and 901, respectively,[13] and cyclobutene by comparison with a published spectrum.[18] The butadiene peak had a shoulder slightly before the main peak of about one-fifth of the total peak area. The retention time of this shoulder corresponded to that of methylcyclopropane,[11] and some weak bands in the infrared spectrum corresponded to those in the infrared spectrum of methylcyclopropane.[19] Another reaction carried out by adding the chloride to sodium in cyclohexane gave in 5% yield a mixture of 1-butene (59%), butadiene (11%, with a small shoulder preceding the main peak), and cyclobutene (30%); Dry Ice was used in the trap so that ethylene would not have been collected.

Acknowledgment.—Preliminary work was supported by Research Grant 7766 from the National Institutes of Health. Recent work has been supported by Grants from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made of this support. We thank Professor Philip S. Skell for the use of g.l.p.c. apparatus, Dr. Garth Tingey for helpful experimental advice, and Bob Peterson and Professor Jennings H. Jones for hydrocarbon samples.

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[12] S. Pinchas, J. Shabtai, and E. Gil-Av, *Anal. Chem.*, **30**, 1863 (1958).

[13] Infrared Spectral Data, American Petroleum Institute, Research Project 44.

[14] S. Pinchas, J. Shabtai, J. Herling, and E. Gil-Av, *J. Inst. Petrol.*, **45**, 311 (1959).

[15] Spectra were taken at 60 Mc. Chemical shifts are in parts per million relative to tetramethylsilane as 10.0.

[16] R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

[17] J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1960).

[18] J. D. Roberts and C. W. Sauer, *ibid.*, **74**, 3192 (1952).

[19] F. E. Condon and D. E. Smith, *ibid.*, **69**, 965 (1947).

Condensation of Dimethyl Acetylenedicarboxylate with Malononitrile, Ethyl Cyanoacetate, and Malonate Esters

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In the presence of a mixture of pyridine and acetic acid, dimethyl acetylenedicarboxylate condenses with malononitrile and with ethyl cyanoacetate to give, respectively, pyridinium salts II and III. Under the same conditions dimethyl acetylenedicarboxylate and malonate esters yield two isomeric 1,1,2,3,4,5,6,7-octacarboalkoxycycloheptadienes. Aqueous potassium acetate converts these cycloheptadienes into the potassium salt of the strongly acidic 1,2,3,4,5-pentacarboalkoxycyclopentadiene.

In his classical studies of the chemistry of acetylenic esters Diels has shown that, in the presence of pyridine and acetic acid, dimethyl acetylenedicarboxylate readily condenses with malononitrile, ethyl cyanoacetate, dimethyl, and diethyl malonate to form a multitude of products.[1] While careful experimental work led to the isolation of a variety of products, disturbing features in several structural assignments prompted our

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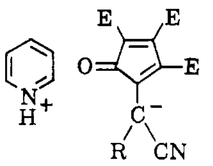
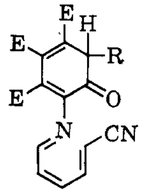
[1] (a) O. Diels, *Chem. Ber.*, **75**, 1452 (1942); (b) O. Diels and U. Kock, *Ann.*, **556**, 38 (1944).

reinvestigation of some of these interesting reactions. As previously reported,[1] dimethyl acetylenedicarboxylate (I) and malononitrile react with equimolar quantities of pyridine and acetic acid to give a blue-black crystalline compound (A), m.p. 205–206°, while I and ethyl cyanoacetate give a deep blue crystalline compound (B), m.p. 171–172°. In accord with Diels we find that A and B result from the condensation of 2 moles of I, 1 mole each of the nitrile and pyridine, less the elements of 1 mole of methanol. However, the strong absorption band in the visible spectrum (668 mμ for A and 625 mμ for B) is wholly incompatible with the unlikely structures IV and V which Diels[1b] suggested for A and B. We propose that the formulations for A and B of II and III are in complete agreement with the chemical and physical properties of the substances. Compound II shows a broad absorption in the visible at 668 mμ. In the infrared nitrile (4.53 μ), ester (5.76 μ), cyclopentadienone carbonyl (5.89, 5.98 μ), and pyridinium cation (6.15, 6.76 μ)[2] are evident.



II, R = CN; E = CO_2Me
III, R = $CO_2C_2H_5$; E = CO_2Me



IV, R = CN; E = CO_2Me
V, R = $CO_2C_2H_5$; E = CO_2Me

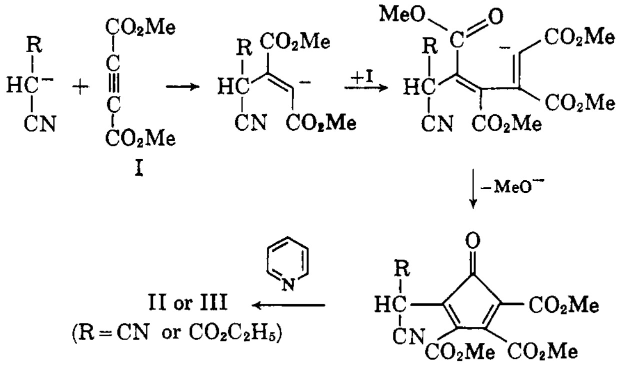
The p.m.r. spectrum of II (Table I) shows a complex multiplet at τ 0.94–2.1 (protonated pyridine) and singlets at τ 6.20, 6.40, 6.41 (methoxy). Compound III exhibits an absorption band in the visible at 625 mμ. The infrared spectrum shows the presence of the nitrile (4.55 μ), ester (5.74 μ), cyclopentadienone carbonyl (5.83, 5.96 μ), and pyridinium (6.12, 6.75 μ).[2] The p.m.r. spectrum of III has a complex multiplet at τ 1.0–2.1 (protonated pyridine), a quartet at τ 5.86 (J = 7 c.p.s., —CH_2—O— of ethoxy group), three singlets at τ 6.25, 6.49, 6.54 (CH_3—O—), and a triplet at τ 8.81 (J = 7 c.p.s., CH_3— of ethoxy). A possible mechanism for the formation of II and III may be envisaged as follows (col. 2).

TABLE I

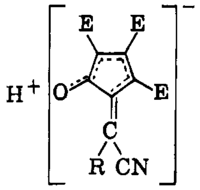
PROTON MAGNETIC SPECTRA[a]

Compound	τ-Values	Multiplicity[b]	Assignment
II[c]	0.94 to 2.1	Complex	Protonated pyridine
	6.20	s	CH_3O—
	6.40	s	CH_3O—
	6.41	s	CH_3O—
III[c]	1.0 to 2.1	Complex	Protonated pyridine
	5.86	q (J = 7 c.p.s.)	—CH_2O— of ethoxy
	6.25	s	CH_3O—
	6.49	s	CH_3O—
	6.54	s	CH_3O—
	8.81	t (J = 7 c.p.s.)	CH_3— of ethoxy

[a] Spectra were obtained on a Varian A-60 spectrometer using chloroform-d as solvent (except where noted) and tetramethylsilane as internal standard. [b] s = singlet, d = doublet, t = triplet, q = quartet. [c] Dimethyl sulfoxide-d_6 used as solvent.

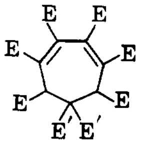


The acids corresponding to these deep blue stabilized carbanions are colorless and quite strong. Spectrophotometric determination of the pK_a gave a value of 1.98 for VI and 2.4 for VII.

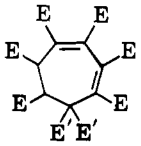


VI, R = CN; E = CO_2Me
VII, R = $CO_2C_2H_5$; E = CO_2Me

In marked contrast to the above reactions, dimethyl acetylenedicarboxylate condenses with dimethyl malonate in the presence of pyridine and acetic acid to give two colorless, pyridine-free isomeric products C, m.p. 225–226°, and D, m.p. 185–187°, as previously reported.[3] While Cookson[4] reported that C was derived from 1 mole of dimethyl malonate and 2 moles of dimethyl acetylenedicarboxylate, the data which we present here, show that C as well as D are derived from 1 mole of malonate ester and 3 moles of dimethyl acetylenedicarboxylate. We propose that C be assigned structure VIII and D be assigned the isomeric structure IX. In accord with these structures are the elemental analyses and molecular weight determinations, which establishes the composition of these isomers as $C_{23}H_{26}O_{16}$. Spectral data on VIII show the presence of ester carbonyl (5.74 μ) and a conjugated diene system (6.17 μ and 284 mμ). The p.m.r. spectrum of VIII (Table II) indicates the presence of the allylic ring proton and four different carbomethoxy groups. In the case of IX spectral data establishes the presence of ester carbonyl (5.75 μ) and a conjugated diene



VIII, E = E′ = CO_2Me
XII, E = CO_2Me; E′ = $CO_2C_2H_5$



IX, E = E′ = CO_2Me
XI, E = CO_2Me; E′ = $CO_2C_2H_5$

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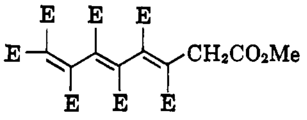
[2] G. M. Barrow, *J. Am. Chem. Soc.*, **78**, 5802 (1956).

[3] While Diels[1a] reported the isolation of both compounds, Cookson and co-workers[4] could not obtain the lower melting isomer. They rationalized their inability to find this substance on the basis that Diels' material was a mixture of esters derived from dimethyl and ethyl methyl malonates which appeared unlikely in view of the 1° melting range reported by Diels.

[4] R. C. Cookson, J. Hudec, and B. Whitear, *Proc. Chem. Soc.*, 117 (1961).

system (6.15 μ and 264 mμ). The p.m.r. spectrum of IX (Table II) indicates the presence of eight carbomethoxy groups in addition to an AX pattern arising from the two different vicinal protons.

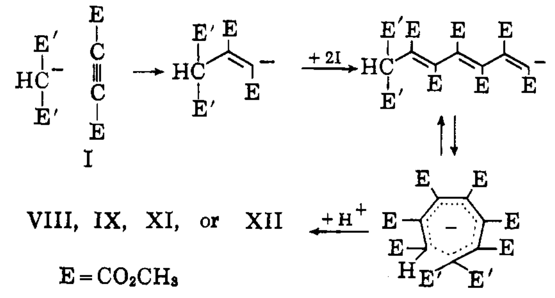
While the p.m.r. spectrum of IX establishes the cyclic system proposed, the data for VIII are also consistent with an acyclic formulation X. That VIII is the correct structure is demonstrated by partially exchanging the allylic ring protons with deuterium. By following this slow exchange in the n.m.r., it was found that the singlet due to the ring proton is not replaced by a triplet as would be expected for the geminal protons of X, but is slowly washed out of the spectrum. Under the same conditions IX isomerized to VIII in a few minutes.


X, E = CO_2Me

VIII proved quite unreactive toward a number of reagents (NBS, bromine, mercuric acetate, selenium dioxide, CH_3CO_2I, tetracyanoethylene, benzyne, hydrogen peroxide–acetonitrile).

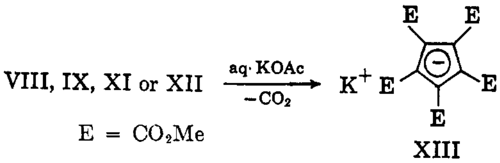
Diethyl malonate also forms two isomeric condensation products with dimethyl acetylenedicarboxylate. The lower melting isomer, m.p. 155–156°, previously isolated by Diels,[1a] has been assigned the structure XI. In addition, careful chromatographic work-up of the residues remaining from the isolation of XI gave the higher melting isomer, m.p. 162–163°, which has been assigned the structure XII. These structural assignments are supported by elemental analyses and molecular weight determinations.[5]

It is apparent that the formation of VIII, IX, XI, and XII involves a mechanism which is rather different from that involved in the formation of II and III.

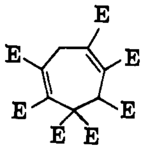

E = CO_2CH_3
E′ = E or $CO_2C_2H_5$

One may speculate that replacement of the nitrile function by carboalkoxy subtly alters the character of the intermediates, either by electronic or steric interactions, to enable addition of a third molecule of the acetylenic ester.

Substantiating earlier findings,[1a] we observed formation of a yellow crystalline compound (E) when VIII and IX are refluxed with aqueous potassium acetate. Furthermore, we find that during this transformation carbon dioxide is evolved (1 mole of carbon dioxide per mole of VIII). Recrystallization of E removes the bright yellow color to give a white crystalline solid, m.p. 219–220°. Elemental analysis established the structure of this compound as XIII, the potassium salt of 1,2,3,4,5-pentacarbomethoxycyclopentadiene.


E = CO_2Me
XIII

In addition to E and carbon dioxide, a moderate quantity of an intractable water-soluble oil can be isolated whose infrared spectrum possessed a broad band in the carbonyl region, plus a trace of a water-insoluble crystalline solid, m.p. 128–129°, which is assigned structure XIV. This assignment is supported by the elemental analysis, molecular weight, infrared spectrum (ester carbonyl and carbon–carbon double bond), ultraviolet spectrum (end absorption with shoulder at 235 mμ), and p.m.r. (Table II) spectrum, which shows the presence of seven different carbomethoxy groups, an allylic ring proton, and an AB quartet arising from the geminal ring protons.


XIV, E = CO_2Me

A clue to the mechanism of this reaction (VIII and IX → XIII) is revealed in our observation that both isomers derived from diethyl malonate, XI and XII, also afforded good yields of potassium salt XIII.[6] It is clear from these results that the fragment lost in this reaction includes the moiety that began as malonate ester. One plausible mechanism suggested by these data involves the removal of a ring proton by base (acetate), an internal Michael reaction followed by rearrangement and cleavage to XIII and tricarboalkoxyethylene. Hydrolysis and decarboxylation of the triester would account for the carbon dioxide observed.

Treatment of the potassium salt (XIII) with hydrochloric acid, gives good yields of the acidic compound 1,2,3,4,5-pentacarbomethoxycyclopentadiene (XV), m.p. 149–150°.[1,3] Elemental analysis and neutralization equivalent are in accord with the formula $C_{15}H_{16}O_{10}$. The infrared spectrum indicates the presence of ester carbonyls (5.80 μ) as well as carbon–carbon unsaturation (6.27 μ). The p.m.r. spectrum consists of a sharp singlet at τ 6.07 indicating the equivalence of the carbomethoxy groups. The singlet expected for the acidic proton in XIII has eluded detection in a

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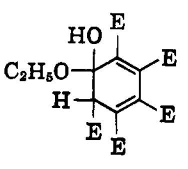
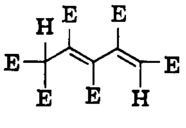
[5] The low values obtained by Diels[1a] for the molecular weight of XI led him to formulate 1:2 malonate-acetylenic ester condensation products with the general structure (i). Cookson and co-workers[4] have assumed that these low values were correct and thus, formulate VIII as ii.


i, E = CO_2Me


ii, E = CO_2Me

[6] Diels reported that, in contrast to VIII and IX, XI upon refluxing with aqueous potassium acetate gave malonate ester.

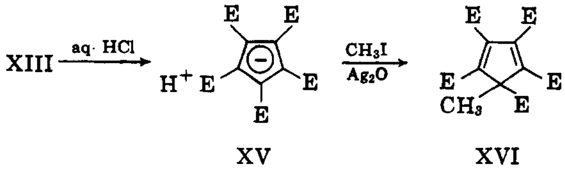
TABLE II

PROTON MAGNETIC SPECTRA[a]

Compound	τ-Values	Multiplicity[b]	Relative area (no. of protons)	Assignment
VIII	4.95	s	1.8	Allylic proton
	6.12	s	6.0	CH_3—O—
	6.26	s	18.0	CH_3—O—
	6.30	s		CH_3—O—
	6.32	s		CH_3—O—
IX	4.88	d (J = 1.5 c.p.s.)	2.2	Allylic proton
	5.31	d (J = 1.5 c.p.s.)		Proton on satd. C
	6.17	s	2.8	CH_3—O—
	6.23	s	5.9	CH_3—O—
	6.29	s	15.0	CH_3—O—
	6.32	s		CH_3—O—
XI	4.88	d (J = 1.6 c.p.s.)	1.2	Allylic proton
	5.33	d (J = 1.6 c.p.s.)	1.2	Proton on satd. C
	5.5–6.1	Complex[c]	22.2	—CH_2—O— of ethoxy
	6.17	s		CH_3—O—
	6.23	s		CH_3—O—
	6.28	s		CH_3—O—
	6.32	s		CH_3—O—
	8.69	t (J = 7.1 c.p.s.)	6.0	CH_3— of ethoxy
	8.73	t (J = 7.1 c.p.s.)		CH_3— of ethoxy
XII	4.95	s	2.0	Allylic proton
	5.82	q (J = 3.7 c.p.s.)	4.1	—CH_2—O— of ethoxy
	5.84	q (J = 3.6 c.p.s.)		
	6.12	s	6.0	CH_3—O—
	6.26	s	6.1	CH_3—O—
	6.32	s	6.0	CH_3—O—
	8.80	t (J = 7.1 c.p.s.)	6.0	CH_3—of ethoxy
XIV	5.13	s	0.8	Allylic proton
	5.78	q (J = 10.6 c.p.s.)	1.8	Allylic geminal protons
	6.17	s	2.9	CH_3—O—
	6.25	s	18.0	CH_3—O—
	6.23	s		CH_3—O—
	6.27	s		CH_3—O—
	6.28	s		CH_3—O—
	6.30	s		CH_3—O—
	6.33	s		CH_3—O—
XV	6.07[d]	s		CH_3—O—
XVI	6.23	s	12.0	CH_3—O—
	6.28	s		CH_3—O
	6.37	s	2.8	CH_3—O
	8.32	s	2.6	CH_3—C

[a] Spectra were obtained on a Varian A-60 spectrometer using chloroform-*d* as solvent and tetramethylsilane as internal standard. [b] s = singlet, d = doublet, t = triplet, q = quartet. [c] Barely discernable are two closely spaced quartets having slightly different coupling constants. [d] In deuterium oxide this singlet was slightly sharper and occurred at τ 6.2.

number of solvents (chloroform-*d*, deuterium oxide, benzene, and nitrobenzene). Presumably, it is either obscured by the methoxy proton absorption or, more likely, it is very broad.



XV XVI

Methyl iodide and silver oxide convert XV into the C-methyl derivative (XVI), m.p. 101–102°. The preparation of XVI from XV with diazomethane as previously reported[4] could not be repeated. This structural assignment is substantiated by the elemental analysis and molecular weight determination as well as the infrared, ultraviolet, and p.m.r. spectra (Table II).

Experimental[7]

Preparation of II.—This salt was prepared according to the method of Diels.[1b] A 60% yield of this blue-black crystalline solid was obtained; m.p. 205–206° (from acetonitrile), lit.[1b] m.p. 201–202°; λ_{max}^{KBr} 3.38, 4.53, 5.76, 5.89, 5.98, 6.15, 6.47, 6.60, 6.72, 6.75, 6.90 μ; λ_{max}^{EtOH} 227 sh mμ (log ϵ 3.93), 257 (4.35), 262 sh (4.33), 313 (4.40), 401 sh (3.68), 668 (3.68).

Anal. Calcd. for $C_{19}H_{15}O_7N_3$: N, 10.58. Found: N, 10.79; pK_a 1.98.

Preparation of III.—Following the method of Diels[1a] there was obtained a 68% yield of the dark blue crystalline salt, III.

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(7) Melting points are corrected. Analyses and molecular weight determinations were carried out in the Mellon Institute microanalytical laboratories and at various commercial laboratories. Molecular weight determinations were made using the thermoelectric osmometer.

Recrystallization from acetonitrile gave analytically pure material; m.p. 171–172°, lit.[1a] 173–174°; λ_{max}^{KBr} 3.28, 3.35, 4.55, 5.72, 5.79, 5.92, 6.09, 6.35, 6.55 μ; λ_{max}^{EtOH} 252 sh mμ (log ϵ 4.29), 257 (4.29), 262 sh (4.25), 317 (4.36), 625 (3.28).

Anal. Calcd. for $C_{21}H_{20}O_9N_2$: C, 56.75; H, 4.54; N, 6.30. Found: C, 57.05; H, 4.63; N, 6.35; pK_a 2.4.

1,1,2,3,4,5,6,7-Octacarbomethoxy-3,5-cycloheptadiene (VIII).—Portionwise addition of 2.5 ml. of equal parts (by weight) of pyridine and acetic acid to a stirred solution of 38 g. (0.27 mole) of dimethyl acetylenedicarboxylate and 11.7 g. (0.09 mole) of dimethyl malonate in 60 ml. of absolute ether resulted in an exothermic reaction. After the vigorous reaction had subsided the dark red mixture was refluxed for 2 hr. (It was necessary to break up the reaction product which formed a solid mass at the bottom of the reaction flask.) This solid was collected, washed with ether, and dried. Most of this material was dissolved in a minimum volume of methanol. The insoluble portion (2 g.), which is impure IX, was collected and worked up according to the description in the next experiment. Chilling the filtrate gave a white crystalline solid 25.9 g., m.p. 225–226°, lit.[1a] m.p. 226°. Further cooling afforded a second crop of 5.0 g., m.p. 223–225° (total yield, 63%). Recrystallization from methanol gave an analytical sample; m.p. 226–227°; λ_{max}^{Nujol} 3.33, 3.40, 3.54, 5.74, 6.17 μ; λ_{max}^{MeOH} 211 mμ (log ϵ 3.94), 284 (3.62).

Anal. Calcd. for $C_{23}H_{26}O_{16}$: C, 49.47; H, 4.70; mol. wt., 558.4. Found: C, 49.48; H, 4.71; mol. wt., 536.

Deuterium exchange was carried out by warming a solution of VIII in acetic acid-*d* containing a trace of pyridine.

1,1,2,3,4,5,6,7-Octacarbomethoxy-4,6-cycloheptadiene (IX).—The 2 g. (4% yield) of insoluble material from the preceding experiment, m.p. 185–187°, was recrystallized from a large volume of methanol with no change in its melting point; lit.[1a] m.p. 182–183°; $\lambda_{max}^{HCCl_3}$ 3.33, 3.40, 5.75, 6.15, 6.96 μ; λ_{max}^{MeOH} 228 mμ (log ϵ 3.94), 264 (3.60).

Anal. Calcd. for $C_{23}H_{26}O_{16}$: C, 49.47; H, 4.70; mol. wt., 558.4. Found: C, 49.72; H, 4.88; mol. wt., 556.

1,1-Dicarboethoxy-2,3,4,5,6,7-hexacarbomethoxy-4,6-cycloheptadiene (XI).—To a stirred solution of 6.08 g. (38 mmoles) of diethyl malonate and 16.19 g. (144 mmoles) of dimethyl acetylenedicarboxylate in 25 ml. of ether was added 1 ml. of a solution containing equal volumes of pyridine and acetic acid. A red color formed and an exothermic reaction began. After 15 min. the reaction had subsided. The mixture was refluxed for 1.25 hr., then allowed to stand at room temperature overnight. The solid, which precipitated (~16 g.), was collected, dried, and stirred with a solution of 50 ml. of ether and 10 ml. of dioxane. The residual material was filtered from the solution (this solution contains XII) and crystallized from methanol to give 3.2 g. (14%) of a white crystalline solid, m.p. 150–152°. Four recrystallizations from methanol gave 1.5 g. of analytically pure material; m.p. 155–156°, lit.[1a] m.p. 154–155°; $\lambda_{max}^{HCCl_3}$ 3.40, 5.75, 6.15, 6.95 μ; λ_{max}^{EtOH}. 215 sh mμ (log ϵ 4.08), 275 sh (3.67), 263 (3.77).

Anal. Calcd. for $C_{25}H_{30}O_{16}$: C, 51.20; H, 5.16; mol. wt., 586.4. Found: C, 51.43; H, 5.26; mol. wt., 574.

1,1-Dicarboethoxy-2,3,4,5,6,7-hexacarbomethoxy-3,5-cycloheptadiene (XII).—The dioxane–ether solution and the various mother liquor from the recrystallizations of XI were combined, concentrated, and chromatographed two times on silicic acid (chloroform eluent). An oil resulted, which was crystallized from methanol. A second recrystallization gave 6.45 g. (29%) of white crystals, m.p. 161–162°. A further recrystallization gave an analytical sample; m.p. 162–163°; $\lambda_{max}^{HCCl_3}$ 3.40, 5.75, 6.14, 6.96 μ; λ_{max}^{EtOH} 215 sh mμ (log ϵ 3.96), 285 (3.61).

Anal. Calcd. for $C_{25}H_{39}O_{16}$: C, 51.20; H, 5.16; mol. wt., 586.5. Found: C, 50.91; H 5.22; mol. wt., 543.

1,2,3,4,5-Pentacarbomethoxycyclopentadienyl Potassium (XIII).—A mixture of 100 g. (0.18 mole) of VIII and 500 ml. of water containing 165 g. of potassium acetate was refluxed for 2 hr. with vigorous stirring. Carbon dioxide was evolved and a clear yellow solution was obtained. This hot solution was filtered and then allowed to cool. A yellow crystalline solid formed (62 g.) which may be converted to the free acid (XV) as described in the next experiment. Thorough washing of the crude yellow solid affords 50 g. (62%) of a pale yellow crystalline solid, m.p. 217–218°. A white crystalline analytical sample was prepared by crystallizing this material from ethanol, m.p. 219–220°.

Anal. Calcd. for $C_{15}H_{15}O_{10}K$: C, 45.68; H, 3.84. Found: C, 45.78; H, 3.85.

A second white crystalline form, m.p 185–186°, was obtained when chloroform–acetonitrile mixture was used for crystallization.

1,2,3,4,5-Pentacarbomethoxycyclopentadiene (XV).—A solution of 5 g. (0.013 mole) of the potassium salt (XIII) in 25 ml. of water was filtered[8] and concentrated hydrochloric acid added until precipitation of the white solid was complete. This material was collected and dried overnight *in vacuo* to give 4.0 g. (90%) of a white solid, m.p. 148–150°, lit.[1a] m.p. 147–148°. An analytical sample was prepared by crystallizing this material from methanol; m.p. 149–150°; $\lambda_{max}^{HCCl_3}$ 5.80, 6.27 μ; λ_{max}^{MeOH} 262 mμ (log ϵ 4.69), 295 (4.16).

Anal. Calcd. for $C_{15}H_{16}O_{10}$: C, 50.56; H, 4.53; neut. equiv., 356. Found: C, 50.54; H, 4.47; neut. equiv., 365.

Both XI and XII gave clear yellow solutions after refluxing and stirring with an aqueous solution of potassium acetate for 2 and 8 hr., respectively. The cooled solutions deposited XIII, which afforded, in both cases, a 69% yield of XV, m.p. 149–151° (mixture melting point with XV obtained from VIII was not depressed and infrared spectra were identical).

1-Methyl-1,2,3,4,5-pentacarbomethoxycyclopentadiene (XVI).—A mixture of 250 mg. (0.70 mmole) of XV, 250 mg. of silver oxide, 0.25 ml. of methyl iodide in 10 ml. of methanol was refluxed for 24 hr. The precipitate was removed and the filtrate refluxed for 12 hr. with a second portion of 250 mg. of silver oxide and 0.25 ml. of methyl iodide. This was repeated a third time. Evaporation of the filtrate left a solid residue which was crystallized from methanol, to give 170 mg. (66%) of a white crystalline solid, m.p. 100–101°. An analytical sample was prepared by an additional recrystallization from methanol; m.p. 101–102°, lit.[3] m.p. 102–103°; $\lambda_{max}^{HCCl_3}$ 3.31, 3.37, 5.73, 6.13, 6.33, 6.93 μ; λ_{max}^{MeOH} 220 mμ (log ϵ 3.95), 292 (3.80).

Anal. Calcd. for $C_{16}H_{18}O_{10}$: C, 51.89; H, 4.90; mol. wt., 370.3. Found: C, 51.79; H, 4.88; mol. wt., 360.

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(8) The insoluble residue (220 mg.), which was collected, was crystallized from methanol to give a white crystalline solid, XIV; m.p. 128–129°; $\lambda_{max}^{HCCl_3}$ 3.33, 3.42, 5.74, 6.06, 6.94 μ; the ultraviolet spectrum showed only end adsorption with a shoulder at 235 mμ (log ϵ 3.95). *Anal.* Calcd. for $C_{21}H_{24}O_{14}$: C, 50.39; H, 4.83; mol. wt., 500. Found: C, 50.52; H, 4,77; mol. wt., 508.