Dicarbanionic and Electron-Transfer Reactions of Cyclooctatetraene Dianion[1,2]

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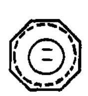
Abstract: The reactions of dilithium cyclooctatetraenide (**1**) with esters and anhydrides have been compared with those of corresponding acid chlorides. The behavior of **1** with select acid chlorides, nitriles, and nitroso compounds has also been investigated. Ethyl acetate and methyl benzoate undergo 1,4 bicyclization of **1** with steric control to yield primarily *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**10**) and *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**14**), respectively. Inverse addition is much more efficient than is normal addition. Acetic anhydride converts **1** to **10** and *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**11**). Benzoic anhydride behaves similarly with **1** to give **14** and *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (**15**); 1,2 biscondensation and isomerization to *trans,trans,trans,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (**26**) is minor. With diethyl phthalate, **1** behaves as a 1,2-dicarbanionic reagent to give 9-(2-carboxyphenyl)-9-hydroxybicyclo[6.1.0]nonatriene lactone (**19**); reaction of phthalic anhydride and **1** and acidification results, however, in 1,4 bridging of **1** and formation of 9-(2-carboxyphenyl)-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene lactone (**29**). 1,2-Biscondensation of **1** and valence isomerization occur upon reaction with ethyl formate and with diethyl oxalate; 2,4,6,8-decatetraene-1,10-dial (**23**) and diethyl 2,11-dioxo-3,5,7,9-dodecatetraenedioate (**24**) are produced. Cyclooctatetraenide **1** is a 1,4-bridging reagent in reaction with phenylacetyl chloride, yielding *syn*-9-hydroxy-9-benzylbicyclo[4.2.1]nona-2,4,7-triene (**30**); methyl chloroformate, however, converts **1** to dimethyl 2,4,6,8-decatetraenedioate (**32**). Benzonitrile is trimerized by **1** to 2,4,6-triphenyltriazine (**34**). Oxidation–reduction occurs in the reaction of **1** and *p*-nitroso-*N*,*N*-dimethylaniline in that cyclooctatetraene and 4,4′-azobis[*N*,*N*-dimethyl]aniline are formed; analogously, **1** is converted by *N*-nitrosodiphenylamine to cyclooctatetraene and diphenylamine. Various metal cations are reduced to metals by **1**.

Cyclooctatetraene dianion (**1**, dilithium cyclooctatetraenide) is of value in synthesis as a dicarbanion (**1a** and **1b**)[3] and as an electron-transfer[3c,d,4] reagent. One of the more striking conversions of **1** (eq 1, 2, and



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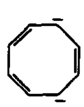
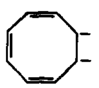


1a



1b

3) is by carboxylic acid chlorides[3d] to give 7-acylcyclooctatrienyl anions **2** which undergo (1) bicyclization to **3** and then acylation and/or protonation to *syn*-9-acyloxy (**4**)[5] and/or *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-trienes[5] (**5**), (2) *vicinal* acylation to 7,8-diacyl-1,3,5-cyclooctatrienes (**6**) and subsequent 1,8-diacyl-1,3,5,7-octatetraenes (**7**), and (3) bicyclization to **8** and acylation to 9-acyloxybicyclo[6.1.0]nona-2,4,6-trienes (**9**). Dianion **1** also reacts as a 1,4- and a 1,2-dicarbanionic reagent with aldehydes and ketones[3e] to yield 5,8-bis(α-hydroxyalkyl)-1,3,6-cyclooctatrienes and 7,8-bis(α-hydroxyalkyl)-1,3,5-cyclooctatrienes; the 1,3,5-cyclooctatrienes isomerize to 2,4,6,8-decatetraene-1,10-diols and 7,8-bis(α-hydroxyalkyl)bicyclo[4.2.0]octadienes.[3e]

A study has now been made of dicarbanionic and electron-transfer reactions of **1** with esters, anhydrides, select acid chlorides, nitriles, and nitroso compounds. The behavior of these systems is compared where appropriate with that of **1** with carboxylic acid chlorides[3d] or with aldehydes and ketones.[3e] In the present investigation the effects of normal and of inverse addition of **1** to the above substrates have been determined. The results of attempts to modify the dicarbanionic behavior of **1** by various metallo cations are also reported.

Results and Discussion

Esters. Dilithium cyclooctatetraenide (**1**) in ether, upon *normal addition* to excess ethyl acetate in ether at 0° and neutralization, yields (Scheme I, eq 1) *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**10**, 31%),[6] *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**11**, trace amounts), and intractables. Addition of ethyl acetate (*inverse addition*) to **1** at 0° is of real advantage in that (1) intermolecular condensation of anionic intermediate **2** (R = CH_3) with additional ethyl acetate is greatly reduced, (2) bicyclization of **2** (R = CH_3) with steric control is enhanced to give **3** (R = CH_3) and subsequently alcohol **10** (77%) upon acidification and (3) acylation of **3** (R = CH_3) to yield ester **11** is very minor under these conditions. 3,5,7,9-Dodecatetraene-2,11-dione (**12**; eq 2) and 9-acetoxy-9-methylbicyclo[6.1.0]nonatriene (**13**; eq 3), products of reaction of acetyl chloride with **1** as a 1,2-dicarbanionic reagent, were not formed from **1** and ethyl acetate.

Reaction of **1** with methyl benzoate is similar to that with ethyl acetate at 0° in that (1) inverse addition is

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[1] Abstracted in part from the Ph.D. Dissertation of T. A. Antkowiak, The Ohio State University, Columbus, Ohio, 1968.

[2] Acknowledgment for support of this research is made to the Office of Ordnance Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

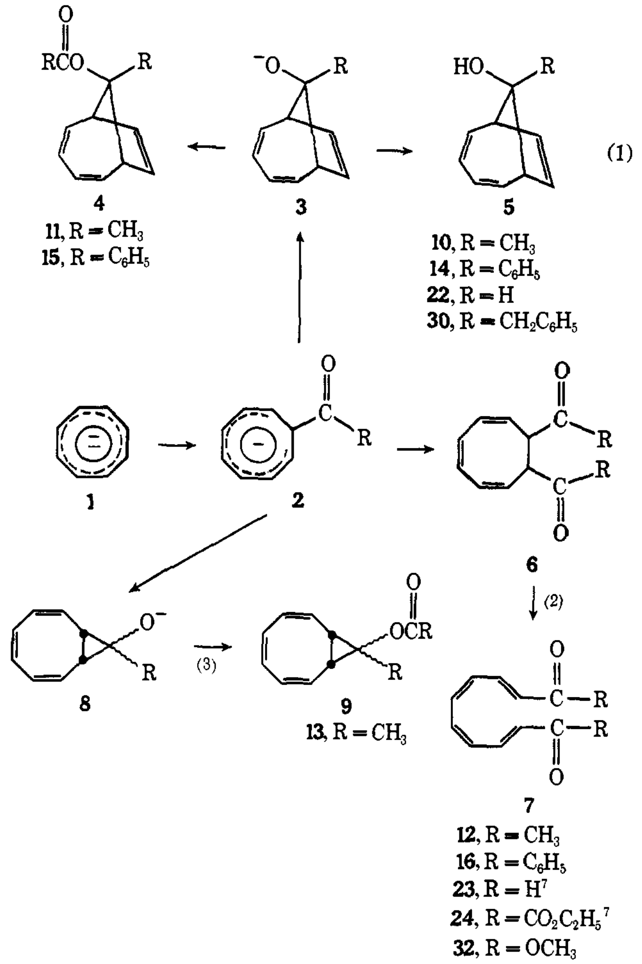
[3] (a) T. J. Katz and P. J. Garrett, *J. Amer. Chem. Soc.*, 86, 5194 (1964); (b) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *ibid.*, 88, 3832 (1966); (c) K. H. Conrow and D. A. Bak, *J. Org. Chem.*, 31, 3958 (1966); (d) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, 89, 5868 (1967); (e) T. S. Cantrell and H. Shechter, *ibid.*, 89, 5877 (1967); (f) T. S. Cantrell, *ibid.*, 92, 5480 (1970); and (g) the many references in the above publications.

[4] (a) K. Conrow and P. C. Radlick, *J. Org. Chem.*, 26, 2260 (1961); (b) M. L. Kaplan and R. W. Murray, *ibid.*, 31, 962 (1966).

[5] In the present manuscript syn stereochemistry indicates that the designated 9 substituent is cis to the diene bridge.

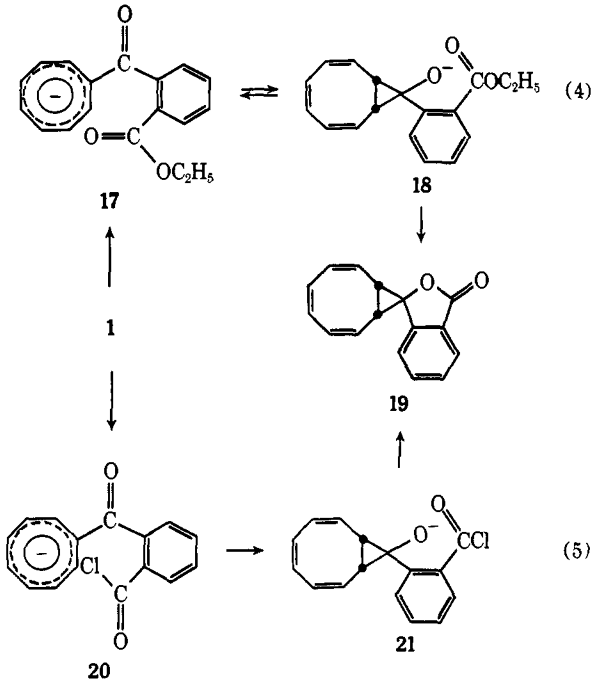
[6] Previous synthesis and proof of structure of this compound have been described in ref 3d.

Scheme I



much the better procedure, (2) bicyclization of **2** (R = C_6H_5) occurs to give *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene[6] (**14**, 74%; eq 1) efficiently, and (3) bicyclo[6.1.0]nona-2,4,6-triene derivatives are not obtained. Normal addition results in extensive polycondensation along with alcohol **14** (21%). Methyl benzoate thus differs from benzoyl chloride in reaction with **1**[6] in that formation of *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene[3d] (**15**, 62%; eq 1) and 1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (**16**; eq 2) is avoided.

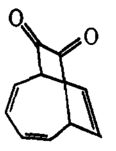
Normal addition of **1** to diethyl phthalate at −60° in ether results in 1,2 bicyclization of **17** to yield 9-(2-carboxyphenyl)-9-hydroxybicyclo[6.1.0]nonatriene lactone[6] (**19**, 15%; eq 4) and polycondensation products. Inverse addition of diethyl phthalate to **1** at 5 or at −60° yields only intractable products. Lactone **19** is identical with the principal product of reaction of phthaloyl chloride and **1**[3d] (eq 5), a much more efficient process. In the advantageous conversion of phthaloyl chloride by **1**[3d] to **19**, bridged monoanionic intermediate **21** has a relatively excellent leaving group and ring closure can occur rapidly with displacement of chloride ion to give **19** as a product of kinetic control. In the reaction of **1** with diethyl phthalate, lactonization of **18** is expected to occur slower than **21** because ethoxide is a poorer leaving group and because of steric factors. Intermediate **18** may thus undergo extensive competitive reactions with diethyl phthalate and/or **1** to yield condensation products.



Reaction of **1** with ethyl formate was investigated as a possible synthesis of *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**22**; eq 1). Addition of ethyl formate at 5 or at −60° to **1** yields, after hydrolysis and isolation, only intractables. By reverting to normal addition of **1** to excess ethyl formate at −60°, 2,4,6,8-decatetraene-1,10-dial (**23** and/or its geometric isomers, 25%; eq 2)[7] along with alcohol **22** (trace amount; eq 1) are obtained. Tetraenedial **23** was isolated as a crystalline yellow solid which melted over a wide range despite repeated recrystallizations. The infrared spectrum of the dialdehyde exhibits carbonyl absorption at 1675 cm^{-1} (conjugated aldehyde) and an olefinic band at 1610 cm^{-1}. Its nmr consists only of a complex multiplet in the olefinic region (τ 2.14–3.92, area = 8) and a doublet due to aldehyde protons (τ 0.31, area = 2). Ultraviolet maxima occur at 223, 345, and 357 mμ (ϵ 4,560, 45,100, and 41,400, respectively). On the basis of its analytical and physical properties, the tetraenedial product is a mixture of geometric isomers. *trans,cis,cis,trans*-Dial **23** is expected as the product of 1,2 biscondensation of **1** with ethyl formate followed by valence tautomerization of **6** (R = H) as in eq 2. Subsequent acidic exposure and/or thermolysis probably resulted in partial isomerization of the initial dial **23**, thus leading to the mixture of isomers.

Reaction of **1** with diethyl oxalate at −60° also results in 1,2 biscondensation of **2** (R = $CO_2C_2H_5$) and valence tautomerization of **6** (R = $CO_2C_2H_5$) to give the acyclic tetraene, diethyl 2,11-dioxo-3,5,7,9-dodecatetraenedioate (**24**; eq 2). A desired diketone, bicyclo[4.2.2]deca-2,4,7-triene-9-10-dione (**25**), was not found. Products from intramolecular cyclization of **2** (R = $CO_2C_2H_5$) are not obtained by either normal or inverse reaction of **1** and ethyl oxalate at 5 or at −60°. The assignment of the structure of **24** is allowed from its analysis, infrared absorption (1685 cm^{-1} for conjugated ester carbonyl), ultraviolet maxima (λ_{max} 228, 286, and 390 mμ (ϵ 5,100, 6,560, and 42,700, respectively)), and nuclear magnetic resonance (τ 2.65–3.24 (m,

(7) The stereochemistry of this product is not known.



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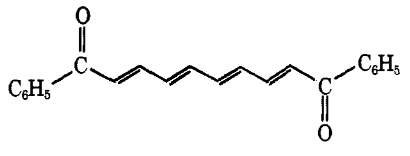
HC=CH, area 8), 5.64 (q, OCH_2CH_3, area 4), and 8.60 (t, CH_3, area 6)).

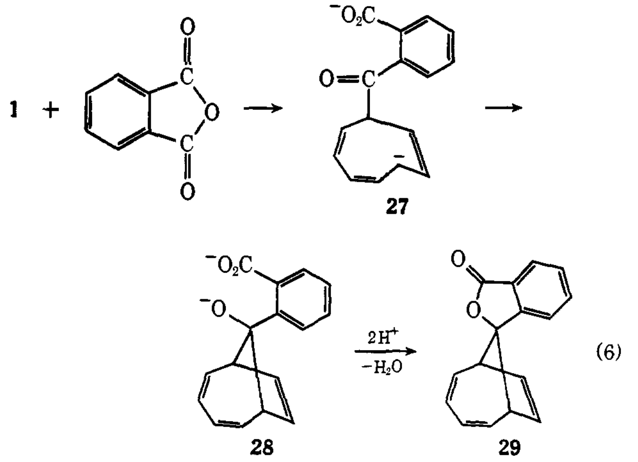
Anhydrides. Acetic anhydride in ether on addition to **1** at 5° results in 1,4 bicyclization to give **3** (R = CH_3) which acylates in part to ester **11**[6] (23%); the remaining **3** is converted upon acidification to alcohol **10** (39%). Acetic anhydride thus behaves much as does acetyl chloride with **1**.[3d] For direct synthesis of alcohol **10**, ethyl acetate is superior because **1** is not converted under the reaction conditions to **11**, **12**, or **13** (equations 1–3).

Inverse addition of benzoic anhydride (2 equiv) to **1** at 36° and acidification yields ester **15** (51%; eq 1), the product of 1,4 bridging of **1**, and benzoylation of **3** (R = C_6H_6). At 0° with benzoic anhydride in equivalent quantity, **1** is converted, after neutralization, to alcohol **14** (52%; eq 1); under these conditions benzoylation of **3** (R = C_6H_5) is repressed. At −60° *trans,trans,trans,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione[3d] (**26**, 4%; eq 2) is formed along with **14** (43%; eq 1) from benzoic anhydride (inverse addition, 1 equiv) and **1**. Reaction of **1** with benzoic anhydride is thus similar to that with benzoyl chloride in that (1) benzoylation of **2** (R = C_6H_5) occurs to give 1,2-dibenzoylcyclooctatriene (**6**, R = C_6H_5) which undergoes valence tautomerization (eq 2) and geometric isomerization to **26**, and (2) greater than 1 equiv of benzoic anhydride leads to benzoylation of **3** (R = C_6H_5) yielding **15**. Satisfactory conversion of **1** by benzoic anhydride to alcohol **14** may be effected by use of appropriate amounts of the anhydride and proper temperature control. Methyl benzoate, a less reactive benzoylating agent, is, however, more efficient for converting **1** to alcohol **14**.



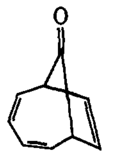
Addition of phthalic anhydride to **1** at 5° and acidification results in 1,4 bridging involving **1** to give 9-(2-carboxyphenyl)-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene lactone (**29**, 48%; eq 6) of indicated stereochemistry. The structure of **29** is assigned on the basis of spectral and analytical evidence. Infrared absorption by **29** at 1765 cm^{-1} is indicative of its lactone carbonyl. Ultraviolet maxima are displayed for 1,3,7-cyclooctatriene[3d] (λ_{max} 244 (ϵ 6990)) and benzoyl (λ_{max} 274 (ϵ 6700)) chromophores. The nmr spectrum (τ 2.36 (m, phenyl H, area 4), 3.86 (m, H at C-2, -3, -4, and -5, area 4), 4.44 (d, H at C-2 and -3, area 2), and 6.86 (m, bridgehead *H*)) confirms the gross structure proposed. The stereochemistry assigned to **29** is based on the expectation that steric interference upon ring closure will be less with the 2-phenyl carboxylate anti rather than syn to the four-carbon diene bridge.

The behavior of **1** with phthalic anhydride is thus decidedly different from that with phthaloyl chloride[3d] and with diethyl phthalate. A significant feature in the reaction of **1** with phthalic anhydride is that addition results in dianionic intermediates **27** and **28** in which the carboxylate group is essentially inert. Ring closure occurs to give the thermodynamically favored dianionic intermediate **28** which upon acidification undergoes rapid lactonization to **29**.



Acid Chlorides. A limited investigation has been made of reactions of **1** with acid chlorides by inverse addition. Phenylacetyl chloride in ether by this method yields *syn*-9-hydroxy-9-benzylbicyclo[4.2.1]nona-2,4,7-triene (**30**, 60%; eq 2). The assignment of the structure of **30** was made from analytical and spectral data. The infrared spectrum of **30** indicates the presence of a hydroxyl group (3700 and 1125 cm^{-1}; C–H and C–O stretching). The ultraviolet spectrum (λ_{max} 220 (ϵ 6600), 264 (ϵ 4780)) is in accord with that of other bicyclo[4.2.1]nona-2,4,7-trienes.[3d] The nmr spectrum conclusively confirms the structural assignment as **30**: τ 2.77 (s, C_6H_5, area 5), 4.00 (m, olefinic *H* on C-2, -3, -4, and -5, area 4), 4.70 (d, olefinic *H* on C-7 and -8, area 2), 6.99 (s, $CH_2C_6H_5$, area 2), 7.15 (m, bridgehead *H*, area 2), and 7.75 (s, O*H*, area 1). The stereochemistry, with the hydroxyl group syn to the diene segment, is inferred on the basis of steric factors during ring closure to the bicyclic system. As in all earlier cases of bridging reactions of **2**, the smaller group (oxygen as opposed to benzyl) lies above the four-carbon bridge.

Methyl chloroformate and **1** were studied at −60° as a possible synthesis of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**31**). Reaction yields, however, the acyclic tetraene, dimethyl 2,4,6,8-decatetraenedioate (**32**, 28%; eq 2). A complex nmr multiplet (τ 2.00–4.20, –HC=CH–, area 8) and a sharp singlet (τ 6.20, $2CH_3$, area 6) reveal the ring-opened structure of **32**. The structural assignment of **32** is also indicated by its ultraviolet (λ_{max} 248, 331, and 345 mμ (ϵ 9,380, 45,700, and 43,300, respectively)) and infrared (>C=O at 1710 cm^{-1} and >C=C< at 1615 cm^{-1}) absorptions. The stereochemistry of **32** has not been established.



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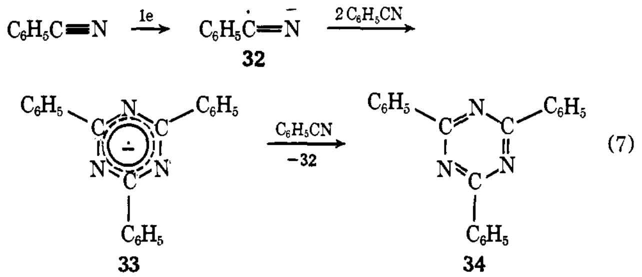
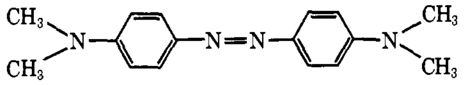
Nitriles. Benzonitrile and **1** react slowly to give 2,4,6-triphenyltriazine (**34**), the symmetrical cyclic trimer of benzonitrile. Products of addition of **1** to benzonitrile were not found. In reaction with benzonitrile, **1** appears to function (eq 7) as an electron-transfer (reducing) reagent yielding benzonitrile radical anion **32**, cyclooctatetraene radical anion, and/or cyclooctatetraene. One attractive possible mechanism for generating **34** involves reaction of **32** with benzonitrile (2 equiv) and electron transfer of the resulting 2,4,6-triphenyltriazine radical anion **33** to an acceptor such as benzonitrile and/or cyclooctatetraene and its radical anion. The previous conversions of benzonitrile by lithium, sodium, diethylzinc, or phenyllithium to **34**[8] are probably related mechanistically to the present system.



32 **33** **34** (7)

Nitroso Compounds. The behavior of **1** with *p*-nitroso-*N*,*N*-dimethylaniline (**35**) was compared to that with aldehydes.[3e] Reaction of **1** and **35** in ether at 10–15° results in 4,4′-azobis(*N*,*N*-dimethyl)aniline (**36**, 56%) and cyclooctatetraene. Formation of **36** from **35** apparently is a result of **1** functioning as a reducing agent rather than by addition to the nitroso group; Grignard reagents function similarly in that they convert **35** to **36**.[9]



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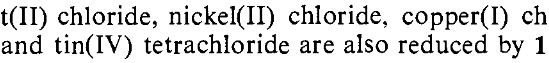
Dilithium cyclooctatetraenide (**1**) also behaves as an electron-transfer reagent in reaction with *N*-nitrosodiphenylamine in that diphenylamine and cyclooctatetraene are formed.

Metal Cations. In an effort to lessen the reactivity of cyclooctatetraene dianion by changing its cation, the behavior of **1** with various metal salts has been investigated. Addition of cadmium chloride to **1** results in formation of metallic cadmium, cyclooctatetraene, and lithium chloride. The overall reaction represents reduction of metal halide by **1** (eq 8). Zinc chloride, cobalt(II) chloride, nickel(II) chloride, copper(I) chloride, and tin(IV) tetrachloride are also reduced by **1** to their corresponding metals. Advantageous procedures could not be developed for effecting reaction of carboxylic acid chlorides with mixtures of **1** and metal halides.



(8)

Experimental Section

Dilithium Cyclooctatetraenide (1). Dry ether (150 ml) was placed in a three-necked flask equipped with a stirrer, a thermometer, and a condenser connected to a nitrogen line. The system was flushed with nitrogen. Lithium (1% sodium; 0.8 g, 0.11 g-atom) was cut into small pieces and then hammered into sheets on glassine powder paper moist with paraffin. The thin sheets of lithium were held in a nitrogen stream emerging from an open neck of the flask and rapidly cut with scissors into small pieces[10] which fell directly into the ether. The stirred solution was cooled to −70°, and cyclooctatetraene (5.2 g, 0.05 mol) was added all at once. The mixture was stirred at −70° for about 4 hr. The cooling bath was then removed and the solution stirred 12–14 hr under nitrogen. The solution became pale green and contained considerable white precipitate. Sufficient dry ether was added to dissolve the precipitated dianion **1**. Typical preparations gave 60–70% yields of **1** as determined by titration.[11]

Reaction of Ethyl Acetate and 1. Ethyl acetate (8.8 g, 0.10 mol) in dry ether (150 ml) was added in 0.75 hr to stirred **1** (from 0.1 mol of cyclooctatetraene) in ether (300 ml) at 4–8° under nitrogen. The orange suspension was stirred for 0.5 hr while warming to room temperature and then poured into ice water (300 ml) containing acetic acid (8 ml). The aqueous layer was then extracted with ether. The extract was combined with the mother liquor and washed with water, dried over magnesium sulfate, and evaporated. Distillation of the red liquid residue yielded *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**10**, 6.8 g, 0.0459 mol, 76.6% based on 60% conversion of cyclooctatetraene to **1**), bp 36–37° (0.6 mm). Gas chromatography on an 8-ft 30% Silicone rubber (UC-W98, 60-80P) column gave a single peak corresponding to **10**. The infrared spectrum of the product is superimposable with that of authentic **10**.

Dropwise addition of **1** (0.08 mol) in ether (300 ml) to ethyl acetate (0.2 mol) in ether (100 ml) at 5–6° yielded **10** (31%, based on 50% conversion of cyclooctatetraene to **1**) and *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**11**).

Reaction of Methyl Benzoate and 1. Methyl benzoate (13.6 g, 0.1 mol) in dry ether (100 ml) was added in 1.25 hr to stirred **1** (from 0.1 mol of cyclooctatetraene) in ether (300 ml) at 0–5° under nitrogen. The suspension was stirred for 0.5 hr while warming to room temperature and then poured into ice water (300 ml)-acetic acid (8 ml). The reaction mixture was worked up as described for ethyl acetate and **1** and evaporated. Recrystallization of the yellow solid from ethanol gave *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]-nonatriene (**14**, 8.55 g, 74.0% based on 55% conversion of cyclooctatetraene to **1**), mp 105.0–107.0°. Recrystallization from ethanol gave an analytical sample as thick white plates, mp 105.5–107.5°.

Anal. Calcd for $C_{15}H_{14}O$: C, 85.70; H, 6.67. Found: C, 85.64; H, 6.71.

The ultraviolet spectrum of **14** in methanol displays maxima at 222.2 and 268.2 mμ (ϵ 6.420 and 3.970). Alcohol **14** exhibits nmr at τ 2.55 (m, C_6H_5, area 4), 3.78 (m, H on C-2, -3, -4, and -5, area 4), 4.68 (d, H on C-7 and -8, J = 1.8 Hz, area 2), 6.75 (m, bridgehead H, area 2), and 7.35 (s, OH, area 1).

Benzoylation of *syn*-9-Hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (14). Benzoyl chloride (0.21 g, 0.015 mol) and **14** (0.21 g, 0.001 mol) were refluxed in pyridine (15 ml) for 10 hr. The mixture was poured into water and stirred briefly. The water was decanted, and the solid washed with 5% sodium carbonate solution, filtered, and then recrystallized from ethanol. The white solid (**15**, 0.15 g, 45%), mp 123–125°, is identical (melting point and mixture melting point; superimposable ir) with authentic *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**15**).[3d]

Reaction of Diethyl Phthalate with 1. A solution of **1** (from 0.05 mol of cyclooctatetraene) in ether (150 ml) was added to a stirred solution of diethyl phthalate (13.3 g, 0.06 mol) in ether (200 ml) at −60° under nitrogen. After addition (0.75 hr), the solution was stirred at −60° for 1 hr and poured into ice water (300 ml)-acetic acid (5 ml). The reaction product in ether, upon usual work-up, was concentrated. The yellow solid which precipitated was filtered, and the filtrate was stored at 5°. Additional precipitate consisted of a yellow substance plus a small amount of red, silky needles. These red needles were separated by hand and recrystallized from benzene (mp 230–231°); the small amount of material prevented its identification. The remaining yellow solids were recrystallized from benzene–chloroform to give 9-hydroxy-9-(2-carboxyphenyl)-bicyclo[6.1.0]nonatriene (**19**, 1.0 g, 15.2%) as faintly yellow chunky

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[8] C. R. Hauser, *J. Org. Chem.*, **16**, 43 (1951), and references therein.

[9] H. Wieland and F. Kogl, *Ber.*, **55**, 1802 (1922).

[10] Results obtained using unhammered lithium shot were almost as satisfactory.

[11] H. Gilman and R. G. Jones, "Organic Reactions," Vol. VI, Wiley, New York, N. Y., 1951, p 353.

prisms, mp 156–158°. Lactone **19** is identical (melting point, mixture melting point and superimposable ir) with the known compound.[3d]

Reaction of Ethyl Formate and 1. Addition of **1** (from 0.2 mol of cyclooctatetraene) in ether (600 ml) to stirred ethyl formate (30.0 g, 0.4 mol) in ether (150 ml) at −60° was effected in 2 hr under nitrogen. Stirring was continued at −60° for 0.5 hr and for an additional 0.5 hr without the cooling bath. The reaction mixture was poured into a solution of water (300 ml) and acetic acid (10 ml). After extraction, work-up, concentration, and storage at 5°, a solid was obtained which on recrystallization from benzene yielded geometrically isomeric 2,4,6,8-decatetraene-1,10-dial[7] (**23**, 4.4 g, 0.0209 mol, 25%), silky yellow needles, mp 150–157°.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.07; H, 6.17. Found: C, 74.38; H, 6.33.

Distillation of the filtrate yielded cyclooctatetraene and a small quantity of *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**22**) as identified by comparison of its infrared spectrum with that from material prepared much more efficiently by methods to be described.[12]

Reaction of Diethyl Oxalate and 1. Dianion **1** (from 0.02 mol of cyclooctatetraene) in ether (200 ml) was added (2 hr) to stirred diethyl oxalate (32.0 g, 0.22 mol) in dry ether (100 ml) at −60° under nitrogen. The reaction mixture was then poured into ice water (300 ml)–acetic acid (10 ml). Separation, ether extraction, concentration, and recrystallization of the product from benzene–chloroform yielded diethyl 2,11-dioxo-3,5,7,9-dodecatetraenedioate[7] (**24**), mp 158–160°, golden flakes (3.6 g, 12.4% based on 55% conversion of cyclooctatetraene to **24**). Concentration of the filtrate gave a viscous red liquid which was chromatographed on an alumina (neutral, activity 1) column (30 × 350 mm) with benzene-hexane and benzene as eluents. Additional **24** (0.5 g) was obtained along with a thick, red syrup.

Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.75; H, 5.88. Found: C, 62.70; H, 6.01.

Reaction of Acetic Anhydride and 1. Acetic anhydride (15.3 g, 0.15 mol) in ether (75 ml) was added (0.5 hr) under nitrogen to **1** (from 0.5 mol of cyclooctatetraene) in ether (150 ml) at 0–5°. The mixture was stirred 0.75 hr at ∼25°, cooled to 10°, and cold water (20 ml) was added slowly. The aqueous layer was separated and extracted with ether. The extract was combined with the mother liquor, washed with saturated sodium bicarbonate solution and then water, dried ($MgSO_4$), and evaporated to a red oil (thin-layer chromatography showed two compounds). Distillation yielded: (1) almost pure *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**10**, 1.0 g, 0.00676 mol, 22.5% based on 60% conversion of cyclooctatetraene to **1**), bp 36–39° (0.6 mm), which upon gas chromatography yielded a sample whose infrared spectrum is superimposable with that of **10** obtained from ethyl acetate and **1**, and (2) a volatile fraction, bp 56–61° (0.7 mm), which after solidification and upon crystallization from ethanol–water yielded *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (**11**, 2.2 g, 0.0116 mol. 38.6% based on 60% conversion of cyclooctatetraene to **1**), mp 46–48°. The product (melting point, mixture melting point, and superimposable ir) is identical with **11** described previously.

Reaction of Benzoic Anhydride and 1. Procedure 1. A mixture prepared by adding (2 hr) benzoic anhydride (22.6 g, 0.10 mol) in ether (150 ml) to a refluxing solution of **1** (from 0.05 mol of cyclooctatetraene) in ether (150 ml) under nitrogen was refluxed 4 hr. The mixture was cooled to 10° and cold water (∼100 ml) was added. Extraction of the mixture with ether, concentration of the ether extract, filtration of amorphous material, evaporation to dryness, and crystallization of the residue gave *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**15**, 4.8 g, 51% based on 60% conversion of cyclooctatetraene to **1**), mp 123.0–125°; no melting point depression was observed on admixture with authentic **15**.

Procedure 2. Benzoic anhydride (11.3 g, 0.05 mol) in ether (100 ml) was added in 2 hr to **1** (from 0.05 mol of cyclooctatetraene) in ether (150 ml) under nitrogen at 2–4°. The mixture was stirred 2 hr at 25–38° and then ice water (100 ml) was added at 8–10°. Isolation of the product yielded a solid which on crystallization from ethanol yielded *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**15**, 3.0 g, 51.9% based on 35% conversion of cyclooctatetraene to **1**), white plates, mp 105.0–107.0°. The ir spectrum of **15** is identical with that of authentic alcohol.[3d]

Procedure 3. An ether solution (100 ml) of benzoic anhydride (11.3 g, 0.05 mol) was dropped in 1 hr to **1** (from 0.05 mol of cyclooctatetraene) in ether (150 ml) at −60° under nitrogen. The mixture was stirred at −60° for 2.5 hr, warmed to 0°, and then water (100 ml) was added. Extraction of the product with ether, the usual work-up, and concentration yielded a yellow solid which on recrystallization from ethanol was identified as *trans,trans,trans,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (**26**, 0.4 g, 4.2% based on 60% conversion of cyclooctatetraene to **1**), silky yellow needles, mp 199–200°, identical ir and no melting point depression by authentic **26**. Recrystallization of the second crop of crystals from ethanol gave *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nonatriene (**14**, 2.7 g, 42.9%), white plates, mp 105.0–107.0°, identical (melting point, mixture melting point, and ir absorption) with previous **14**.

Reaction of Phthalic Anhydride and 1. Phthalic anhydride (7.0 g, 0.047 mol), partially dissolved in ether (150 ml), was added portionwise in 0.75 hr to stirred **1** (from 0.05 mol of cyclooctatetraene) in ether (150 ml) at 0–5° under nitrogen. The orange colored suspension was stirred under nitrogen for 3 hr at room temperature. The reaction mixture was cooled to 10° and dilute sulfuric acid (11.5 g of concentrated H_2SO_4 in 75 ml of H_2O) was added slowly. The mixture was stirred for 0.25 hr at 5° and then a white solid was filtered. The aqueous layer was separated and extracted with ether. The extract was combined with the mother liquor, washed with water, saturated sodium bicarbonate, and water, dried ($MgSO_4$), and then concentrated under partial vacuum to approximately 50 ml. The solution was cooled and the white solid that precipitated was filtered. This solid was combined with that previously filtered and then recrystallized from benzene–chloroform. A second recrystallization gave the lactone of 9-hydroxy-9-(2-carboxyphenyl)-bicyclo[4.2.1]nona-2,4,7-triene (**29**, 3.4 g, 0.0144 mol, 48% based on 60% conversion of cyclooctatetraene to **1**), chunky white plates, mp 193.0–195.5°.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.36; H, 5.09. Found: C, 81.57; H, 5.31.

Reaction of Phenylacetyl Chloride and 1. Phenylacetyl chloride (15.5 g, 0.10 mol) in ether (75 ml) was added in 0.75 hr to stirred **1** (0.062 mol) in ether (150 ml) at 5° under nitrogen. The orange-red suspension was stirred for 2 hr while warming to 15° and then ice water (200 ml) containing acetic acid (8 ml) was added. The ether extracts of the reaction mixture were washed with water, saturated sodium bicarbonate, and water, dried, and evaporated. The yellow solid obtained, on crystallization from benzene, yielded *syn*-9-hydroxy-9-benzylbicyclo[4.2.1]nona-2,4,7-triene (**30**, 8.3 g, 0.0371 mol, 59.9%), white crystals, mp 94.5–96.5°.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.75; H, 7.14. Found: C, 86.28; H, 7.15.

Reaction of Methyl Chloroformate and 1. A solution of **1** (0.024 mol) in ether (300 ml) was dropped (1 hr) into stirred methyl chloroformate (9.5 g, 0.1 mol) in ether (100 ml) at −60° under nitrogen. The dark brown suspension was stirred for 1 hr at −60°, allowed to warm to room temperature, and stirred overnight. Filtration of the yellow suspension yielded an orange powder which was washed with water and extracted with boiling petroleum ether. Cooling and filtering the petroleum ether suspension gave dimethyl 2,4,6,8-decatetraenedioate (**32**, 1.5 g, 28.1%), orange needles, mp 115–117°.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: C, 64.75; H, 6.38.

Concentration of the filtrate yielded a small quantity of residue which was shown by thin-layer chromatography to contain at least four compounds. The small amount and the complexity of the mixture precluded its identification.

Reaction of Benzonitrile and 1. A solution of **1** (0.018 mol) in ether (150 ml) was added in 1 hr to benzonitrile (15.5 g, 0.15 mol) in ether (100 ml) at 4–6° under nitrogen. The mixture was stirred 2 hr at room temperature, stored overnight, poured into dilute hydrochloric acid, and separated. The aqueous layer was extracted with ether and the ether solutions were combined, washed with water, dried, concentrated, and cooled. The white solid formed, upon crystallization from benzene, was identified as 2,4,6-triphenyltriazine[8] (**34**, 0.5 g, 0.0016 mol, 27% based on one electron transfer from **1**), white needles, mp 233–234.5°, identical (melting point mixture and ir absorption) with an authentic sample.

The filtrate on distillation yielded benzonitrile (>10 g), mixed cyclooctatrienes (1.0 g), and cyclooctatetraene (trace quantity).

Reaction of *p*-Nitroso-*N*,*N*-dimethylaniline and 1. *p*-Nitroso-*N*,*N*-dimethylaniline (27 g, 0.18 mol) in dry tetrahydrofuran (200 ml) was added in 10 min to **1** (0.051 mol) under nitrogen at 10–15°. The dark suspension was stirred at 25–30° for 1 hr and

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(12) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. L. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).

water (100 ml) and then 33% sodium hydroxide solution (6 ml) were added. The mixture was stirred at 25° for 1 hr, heated to 50°, cooled to 5°, and filtered to yield a brown solid (11.7 g). Concentration of the filtrate gave additional solid (3.5 g). The combined solid, upon crystallization from benzene–chloroform, yielded 4,4′-azobis[*N*,*N*-dimethyl]aniline (**36**), bright orange needles, mp 265–268°, identical (melting point, mixture melting point, and ir absorption) with an authentic sample. Distillation (0.5 mm) of the remaining product, a dark viscous oil, resulted in recovery of cyclooctatetraene (5.8 g).

Reaction of *N*-Nitrosodiphenylamine and 1. Dropwise addition of **1** (0.028 mol) in ether (150 ml) was effected under nitrogen to *N*-nitrosodiphenylamine (16.6 g, 0.0838 mol) in ether (150 ml) at 0–5°. The brown suspension was stirred 1 hr without the cooling bath, cooled to 5–10°, and ice water (200 ml)–acetic acid was added. The ether phase and ether extracts of the aqueous solution were combined, washed with water and with aqueous sodium bicarbonate, dried, concentrated, and distilled (0.5 mm). The distillate was shown by glc to be pure cyclooctatetraene.

The black viscous distillation residue was chromatographed on silica gel. Elution with benzene and recrystallization from hexane gave diphenylamine (1.90 g), colorless leaflets, mp 52.5–54.0°, identical (melting point, mixture melting point, and ir absorption) with authentic material. The second compound eluted with benzene was *N*-nitrosodiphenylamine (3.6 g), mp 63.0–66.5°, identical with initial material. Evaporation of methanol washings of the silica gel column yielded an unidentified dark brown amorphous solid.

Reaction of Cadmium Chloride and 1. Cadmium chloride (18.3 g, 0.1 mol), dried at 100° under vacuum for 24 hr, was added (10 min) under nitrogen to stirred **1** (0.056 mol) in ether (150 ml) at 0–5°. The mixture was refluxed 1.75 hr, stored overnight at room temperature, and then poured into cold water (250 ml). The solid that remained on filtration was metallic cadmium (4.3 g, 0.0384 mol, 69%), identified by solution in hydrochloric acid with evolution of hydrogen, evaporation to dryness, dissolution of the white solid in dilute sulfuric acid, and conversion to yellow cadmium sulfide upon addition of 5% thioacetamide.

Distillation of the ether extract of the initial filtrate yielded cyclooctatetraene (~6.0 g, ~0.058 mol, ~100%), bp 40–42° (10 mm), identified by the superimposability of its infrared spectrum with that from authentic material.

Synthesis and Chemistry of Bicyclo[4.2.1]nona-2,4,7-trien-9-one and of Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Intermediates[1,2]

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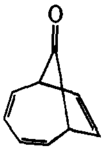
Abstract: Bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**), the bicyclo[4.2.1]nona-2,4,7-triene-9-carbene (**2**), and the bicyclo[4.2.1]nona-2,4,7-triene-9 cation (**3**) have been studied. Dilithium cyclooctatetraenide (**6**) and dimethylcarbamoyl chloride, upon acidification, give **1**. Decarbonylation of **1** to cyclooctatetraene (**12**) occurs upon irradiation; tricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (**13**) and tricyclo[3.3.1.$0^{2,8}$]nona-2,7-dien-9-one (**14**) are minor products. Sensitized photolysis results mainly in carbon-skeleton rearrangement to **14**. Stereochemically controlled nucleophilic addition of phenyllithium and of sodium borohydride occurs with **1** to give *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (**9**) and *syn*-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (**16**). Ketone **1** undergoes acid-catalyzed conversion to its ethylenedithioketal (**20**), oxime (**25**), tosylhydrazone (**26**), and 2,4-dinitrophenylhydrazone (**27**). Ring expansion occurs in the reaction of **1** with diazomethane–lithium chloride to yield bicyclo[4.2.2]deca-2,4,9-trien-7-one (**21**) and spiro[bicyclo[4.2.1]nona-2,4,7-triene-9,2′-oxirane] (**22**). Oxime **25** undergoes Beckmann fragmentation by tosyl chloride in pyridine to give cyano-1,3,5,7-cyclooctatetraene (**28**). Carbene **2**, as generated *via* its diazo precursor **30** from the sodium salt of **26**, isomerizes to indene (**31**). Attempts to generate cation **3** from *syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate (**41**) and di-*syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite (**42**) result in rearrangement and elimination to **31**. Reaction of **41** in tetrahydrofuran with lithium aluminum hydride gives bicyclo[4.3.0]nona-2,4,7-triene (**43**). In boron trifluoride **1** isomerizes to 1-indanone (**50**). The rearrangements of **2** and **3** and of **1** as catalyzed by boron trifluoride have been rationalized on the basis of migration of C-2 or -5 of the diene bridge to C-9 with subsequent reorganization. The possible roles of bicycloaromaticity and degeneracy in reactions of **1**, **2**, and **3** have been considered. The synthetic utility of dimethylcarbamoyl chloride (over phosgene) in reactions with organometallics is described.



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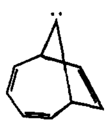

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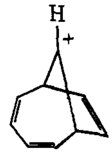

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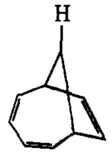

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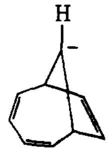

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The bicycloaromatic properties[3a] of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) and its related intermediates, the bicyclo[4.2.1]nona-2,4,7-triene-9-carbene (2),[3a,b] cation 3, radical 4,[3a] and carbanion 5,[3a] are sub-

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(1) Abstracted in part from the Ph.D. Dissertation of T. A. Antkowiak, The Ohio State University, Columbus, Ohio, 1968. This research has also been abstracted in part in *Diss. Abstr. Int. B*, 30, 112 (1969) and *Chem. Abstr.*, 72, 110871d (1970).[1a]

(1a) NOTE ADDED IN PROOF. K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972), have recently communicated a study of thermal and photochemical decomposition of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) in which the results are similar to those of the present report. After our manuscript had been submitted (Oct 13, 1971) to *J. Amer. Chem. Soc.*, we learned (Jan 12, 1972) of the similar study by Kurabayashi and Mukai and immediately transmitted to these investigators a copy of our paper along with prior references[1] to our completed study of the thermal and photochemistry of 1.

(2) Acknowledgment is made for support of this research by the Office of Ordnance Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We should also like to acknowledge very informative discussions on photochemistry with J. S. Swenton and the contribution of M. J. Broadhurst in detecting and identifying **22** in the reaction of diazomethane with 1.

(3) (a) M. J. Goldstein, *J. Amer. Chem. Soc.*, 89, 6359 (1967); (b) R. E. Leone and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 860 (1970).