gas chromatography,[20,21] the calculated yields were 47% **2**, 4% **1**, 22% **3**, and 18% **4**.

Irradiation of 200 mg of **1** in 8 ml of benzene for 9.5 hr followed by gas chromatography[21] showed **3** and **4** to be present in the relative amounts of 45 and 55%, respectively.

Irradiation of 140 mg of **1** in 5 ml of benzene was followed by gas chromatographic analysis[21] at various time intervals to determine the relative amounts of **3** and **4**. The results are listed in Table I.

Table I. Relative Amounts of **3** and **4** during Irradiation of **1**

Time, min	% **3**	% **4**
5	100	0
15	100	0
25	93	7
35	92	8
65	81	19
80	78	22
200	60	40
550	45	55

The nmr and ultraviolet spectra of compounds **2**, **3**, and **4** are described in the text. *Anal.* Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found for **2**: C, 89.42; H, 10.51. Found for a mixture of 55% **3** and 45% **4**: C, 88.71; H, 10.61.[22]

The infrared spectrum of **2** shows a medium band at 3020 cm^{-1} (C–H stretch of olefin) and a weak band at 1640 cm^{-1} (unconjugated double bond).

A 82.3-mg (0.614 mmole) sample of **2** in 10 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 29 mg of platinum oxide. The hydrogen uptake (32.5 cc or 2.1 equiv) ceased after 50 min. The reaction mixture was filtered and concentrated. Gas chromatography[20,23] showed only one peak in addition to the solvent.

A 34.9-mg (0.26 mmole) sample of a mixture of 55% **3** and 45% **4** in 15 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure over the catalyst from 35 mg of platinum oxide. The hydrogen uptake (20.5 cc or 3.1 equiv) ceased after 40 min. The reaction mixture was filtered and concentrated. Gas chromatography[20,21,23] showed only one peak in addition to solvent. The material was collected for analysis. *Anal.* Calcd for $C_{10}H_{20}$: C, 85.62; H, 14.38. Found: C, 85.79; H, 14.18.

Irradiation of 1-Deuterio-3,7,7-trimethylcycloheptatriene (1-*d*₁). A solution of 1.5 g of **1**-*d*₁ was irradiated in 40 ml of benzene as described for the unlabeled compound for 4.5 hr. The reaction mixture was concentrated and samples of **2**, **3**, and **4** were collected by gas chromatography.[20,21]

Photoequilibration of 3 and 4. A. Irradiation of 10 mg of **3** in 0.25 ml of benzene for 8 hr showed **3** and **4** to be present in the relative amounts of 45 and 55%, respectively.

B. Irradiation of 10 mg of **4** in 0.25 ml of benzene for 5 hr showed **3** and **4** to be present in the relative amounts of 40 and 60%, respectively.

Irradiation of 2. A solution of 60 mg of **2** was irradiated in 2 ml of benzene for 24 hr. Gas chromatography[20] showed one peak in addition to solvent having the retention time of **2**.

Irradiation of Trienes 3 and 4. A solution of 40 mg of the trienes (52% **3** and 48% **4**) was irradiated in 2 ml of benzene. After 2 hr, the relative amounts of the trienes were 45% **3** and 55% **4**. This ratio remained unchanged during further irradiation. After 6.5 hr, gas chromatography[20] showed 65% of a new, poorly resolved multiplet containing at least three peaks having retention times very similar to **2**. Irradiation was discontinued after 8.5 hr, at which time gas chromatography[20] showed 95% of new products and 5% of the trienes (still 45% **3** and 55% **4** as determined by gas chromatography[21]). The new products were not investigated further.

Acknowledgment. The authors are grateful to the National Aeronautics and Space Administration for an institutional grant which was used in part to support this work.

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[22] We could not obtain a satisfactory analysis for **3** and **4**, either separately or as a mixture, despite repeated collections and recollections by gas chromatography,[20,21] followed by short-path distillation. Our only conclusion is that the compounds suffer decomposition prior to analysis. The nmr spectra give satisfactory integrations. The ultraviolet spectra were obtained on samples immediately following collection.

[23] A column packed with Carbowax 20M suspended on Chromosorb P was employed.

Cyclic Polyolefins. XLVI. Synthesis of 1,2-Di(hydroxymethyl)cyclooctatetraene and Cyclooctatetraene-1,2-dicarboxylic Acid[1a]

Arthur C. Cope[1b] and Jay E. Meili[1c]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received December 17, 1966*

Abstract: 1,2-Di(hydroxymethyl)cyclooctatetraene and 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid have been synthesized by the copolymerization of acetylene with 2-butyne-1,4-diol diacetate and with dimethyl acetylenedicarboxylate, respectively. The structures of the products were related to the known 1,2-dimethylcyclooctane. Attempted resolution of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid *via* the monoquinine salt and the mono-*d*-α-methylphenethylamine (Dexedrine) salt was unsuccessful.

Substituted cyclooctatetraenes have been synthesized by the copolymerization of acetylene and substituted acetylenes[2] under conditions similar to those employed in the preparation of cyclooctatetraene from acetylene.[3,4]

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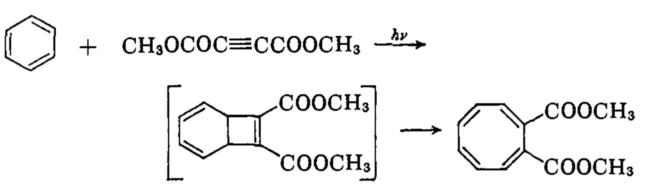
[1] (a) Abstracted from the Ph.D. thesis of J. E. Meili, Massachusetts Institute of Technology, 1952. (b) Deceased June 4, 1966. (c) Author to whom inquiries should be addressed: Plastocon Corp., Oconomowoc, Wis.

[2] A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **73**, 3536 (1951); **74**, 179 (1952).

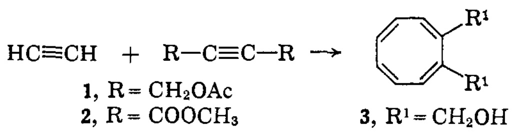
[3] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

[4] A. C. Cope and L. L. Estes, Jr., *J. Am. Chem. Soc.*, **72**, 1129 (1950).

The synthesis of 1,2-substituted cyclooctatetraenes containing functional groups has been accomplished by the photolytic addition of the appropriately substituted acetylene to benzene as in the case of dimethyl cyclooctatetraene-1,2-dicarboxylate.[5,6]



1,2-Di(hydroxymethyl)cyclooctatetraene (**3**) and 2,4,-6,8-cyclooctatetraene-1,2-dicarboxylic acid (**4**) have now been synthesized by the copolymerization of acetylene and 2-butyne-1,4-diol diacetate (**1**) and dimethyl acetylenedicarboxylate (**2**), respectively.



1, $R = CH_2OAc$
2, $R = COOCH_3$
3, $R^1 = CH_2OH$
4, $R^1 = COOH$

2-Butyne-1,4-diol was found not to react with acetylene to form the desired product. The diacetate **1**, when allowed to react with acetylene under conditions designed for copolymerization,[2] afforded a 22% yield of 1,2-di(hydroxymethyl)cyclooctatetraene. The product was isolated from the aqueous phase of the steam distillate by extraction with ether and was separated from the small amount of 1,2-di(hydroxymethyl)benzene (formed from the copolymerization of acetylene and **1** in a 2:1 ratio) by extraction with aqueous silver nitrate. The cyclooctatetraenediol **3** was a hygroscopic oil which was purified by preparation and saponification of the dibenzoate. No 1,2-di(hydroxymethyl)-cyclooctatetraene diacetate was isolated from the reaction mixture; it is assumed that this initial product was hydrolyzed under the conditions used for isolation.

An authentic sample of 1,2-di(hydroxymethyl)benzene was obtained by lithium aluminum hydride reduction of dimethyl phthalate. The material isolated from the copolymerization had an infrared spectrum identical with that of the authentic sample and the mixture melting point was not depressed.

Catalytic hydrogenation of 1,2-di(hydroxymethyl)-cycloctatetraene afforded 1,2-dimethylcyclooctane; this material had identical physical constants with that obtained by catalytic reduction of 1,2-dimethylcyclooctatetraene (prepared by the copolymerization of acetyl ene and 2-butyne). (The hydrogenation product may be a mixture of geometric isomers.)

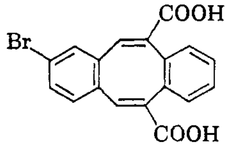
Dimethyl acetylenedicarboxylate (**2**) was allowed to react with acetylene under the conditions previously described.[2] 2,4,6,8-Cyclooctatetraene-1,2-dicarboxylic acid[7] was isolated from the steam distillate as a yellow solid, which was recrystallized from acetonitrile. The dicarboxylic acid ester was not isolated and probably underwent hydrolysis under the conditions of the isolation.

The dicarboxylic acid **4** was related to 1,2-di(hydroxymethyl)cyclooctatetraene by esterification with diazomethane, lithium aluminum hydride reduction to the diol, and conversion to the dibenzoate.

It has previously been mentioned[8,9] that, due to the nonplanarity of the cyclooctatetraene structure, mono- and disubstituted cyclooctatetraenes should possess optical activity unless the nonplanar cyclooctatetraene were readily deformed, for example, by assuming a planar configuration through a bond shift–inversion process, resulting in rapid racemization. Attempts to resolve N,N-dimethyl-4-aminophenylcyclooctatetraene,[8] cyclooctatetraenecarboxylic acid,[9] and 3-cyclooctatetraenylpropionic acid[10] resulted in failure. In the present work, a preliminary attempt to resolve cyclooctatetraene-1,2-dicarboxylic acid was made *via* the monoquinine salt and the mono-*d*-α-methylphenethylamine (Dexedrine) salt. In both cases it was possible to recrystallize the salts to constant optical rotation and melting point. However, in each case the acid regenerated from the salt was optically inactive, indicating that rapid racemization had occurred or that the two salts employed were unsuitable, if the molecule is indeed asymmetric.

Recent low-temperature, nuclear magnetic resonance studies of cyclooctatetraene[11] and substituted cyclooctatetraenes[12,13] have demonstrated that rapid interconversion of the enantiomeric forms occurs. The enthalpy change ($\Delta H^*_{40°}$) for the inversion–bond shift process for ethyl cyclooctatetraenecarboxylate has been found to be 12.8 kcal/mole.[12] If the substituted cyclooctatetraenes upon which resolution was attempted possess activation parameters of this magnitude, optical activity would not be expected to be observed under ordinary conditions.

It should be noted that the optical resolution of the 8-bromodibenzo[*a*,*e*]cyclooctene-5,12-dicarboxylic acid (**5**) has been achieved *via* the brucine salt.[14] The activation energy was determined to be 27 kcal/mole.



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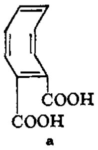
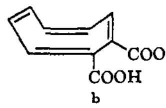
(5) E. Grovenstein, Jr., and D. V. Rao, *Tetrahedron Letters*, 148 (1961).

(6) (a) D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc.*, 333 (1961); (b) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963).

(7) Attempts to form the anhydride of this dicarboxylic acid with acetic anhydride did not succeed, as has also been reported by Bryce-Smith and Lodge.[6b] (This confirms previously unpublished results by J. E. Meili and by P. W. Wegener.) The formation of a relatively strain-free anhydride would be possible only if the molecule had the conformation shown in a. X-Ray crystallographic studies have shown that the calcium salt (as the dihydrate) corresponds to structure b [D. A. Wright, K. Seff, and D. P. Shoemaker, *Acta Cryst.*, **16**, A58 (1963), to be published later in detail] in which the carboxyl groups are skew to each other, and hence we have named the dicarboxylic acid accordingly. In the absence of direct experimental data, 1,2-disubstituted cyclooctatetraenes are assumed to have similar structures in general in order to avoid the eclipsing present in structures like a.



a



b

(8) A. C. Cope and M. R. Kinter, *J. Am. Chem. Soc.*, **73**, 3424 (1951).

(9) A. C. Cope, M. Burg, and S. W. Fenton, *ibid.*, **74**, 173 (1952).

(10) A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953).

(11) F. A. L. Anet, *ibid.*, **84**, 671 (1962).

(12) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).

(13) D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87**, 2862 (1965).

(14) K. Mislow and H. D. Perlmutter, *ibid.*, **84**, 3591 (1962).

However, in this case the benzene rings would be expected to contribute both sterically and electronically to the destabilization of a planar transition state.

Experimental Section[15]

2-Butyne-1,4-diol Diacetate (1). The diacetate was obtained in 80% yield from the treatment of butyne-1,4-diol with acetic anhydride in benzene at the reflux temperature. Distillation through a semimicro column gave a product having bp 105–106° (3 mm), $n^{25}\mathrm{D}$ 1.4519–1.4521, and mp 26.0–27.5° [lit.[16] bp 122–123° (10 mm), $n^{20}\mathrm{D}$ 1.4611, and mp 28°[17]).

1,2-Di(hydroxymethyl)cyclooctatetraene (3). 2-Butyne-1,4-diol diacetate (25 g) and acetylene were copolymerized according to the procedure described previously for the reaction of acetylene with substituted acetylenes.[2] The reaction was carried out for 13 hr at a temperature of 82–93° and an acetylene pressure of 230–325 psi, during which time a total of 950 psi of acetylene was absorbed. Steam distillation of the reaction mixture was continued until 5 l. of distillate had been collected. Cyclooctatetraene (36.2 g) was isolated from this distillate. The aqueous residue from the steam distillation was filtered, and the solution was extracted continuously with ether for 4 days. The dried ether solution was evaporated at reduced pressure to give a light brown oil.

The crude diol (10.81 g) in benzene solution was extracted with three 50-ml portions of aqueous 50% (by weight) silver nitrate. The silver nitrate solution was then continuously extracted with ether for 42 hr. Ammonium hydroxide was added to the cold aqueous silver nitrate solution until the precipitate dissolved and this solution was extracted continuously with ether for 48 hr. This ether extract was dried with sodium sulfate, and the ether was removed at reduced pressure. The resulting yellow oil was distilled in a short-path still (bath temperature 100°, 0.5 mm) to give 5.40 g (22%) of 1,2-di(hydroxymethyl)cyclooctatetraene as a hygroscopic oil, $n^{25}\mathrm{D}$ 1.5712. Purification of the compound was accomplished through the preparation and saponification of the dibenzoate (see below).

The ether extract of the silver nitrate solution, after drying with magnesium sulfate and removal of the solvent under reduced pressure, afforded a dark oil which was crystallized from benzene–*n*-hexane to give a small amount of 1,2-di(hydroxymethyl)benzene having mp 62.0–64.2°. A mixture of this material and 1,2-di(hydroxymethyl)benzene (mp 62.8–64.8°) obtained by reduction of dimethyl phthalate with lithium aluminum hydride melted at 62.6–64.4°.

1,2-Di(hydroxymethyl)cyclooctatraene Dibenzoate. 1,2-Di(hydroxymethyl)cyclooctatetraene (870 mg) in 8 ml of pyridine was treated with 1.82 g of benzoyl chloride. The mixture was stirred for 2 min, heated to the boiling point briefly, and then poured into 10 ml of cold water. The water was removed from the resulting oil by decantation, and the oil was washed with 5 ml of 5% sodium carbonate solution. Upon standing, a precipitate formed which was removed by filtration and washed with three 10-ml portions of water and two 5-ml portions of dilute hydrochloric acid. Two recrystallizations from ethanol–water gave 1.246 g (63%) of the dibenzoate having mp 80.8–83.6°. After five additional recrystallizations the sample had mp 82.0–83.4°.

Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.16; H, 5.38.

Saponification of 1,2-Di(hydroxymethyl)cyclooctatetraene Dibenzoate. The dibenzoate (0.644 g) was added to a solution of 0.5 g of sodium hydroxide in 65 ml of water. The mixture was heated at 80° for 2 hr, and then 0.75 g of sodium hydroxide in 50 ml of water and 75 ml of ethanol were added. After heating at the reflux temperature for 12 hr, the solution was cooled and continuously extracted with ether for 36 hr. Upon distillation, the dried ether solution gave a solid residue which was reextracted several times with ether. Removal of the ether at reduced pressure gave 204 mg (72%) of 1,2-di(hydroxymethyl)cyclooctatetraene. This hygroscopic yellow oil, after distillation three times in a short-path still at 0.5 mm with exclusion of moisture, had $n^{25}\mathrm{D}$ 1.5740.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.94; H, 7.48.

Catalytic Hydrogenation of 1,2-Di(hydroxymethyl)cyclooctatetraene. A solution of 1.19 g of 1,2-di(hydroxymethyl)cyclooctatetraene in approximately 25 ml of glacial acetic acid was shaken with hydrogen in the presence of 400 mg of prereduced platinum oxide catalyst until hydrogen absorption had ceased (10.5 hr). After filtration, the acetic acid solution was diluted with 25 ml of water and extracted with three 25-ml portions of pentane. The pentane solution was dried with potassium carbonate and the pentane was distilled through a 1.5 × 25 cm column packed with glass helices. Distillation of the residual oil through a semimicro column afforded 588 mg of 1,2-dimethylcyclooctane, bp 98–99° (66 mm), $n^{25}\mathrm{D}$ 1.4570–14579. The physical constants and infrared spectrum of this material were in agreement with those of an authentic sample.[18]

2,4,6,8-Cyclooctatetraene-1,2-dicarboxylic Acid (4). Dimethyl acetylenedicarboxylate (25 g) was copolymerized with acetylene under the conditions described above for the synthesis of 1,2-di(hydroxymethyl)cyclooctatetraene. The reaction was carried out for 10.5 hr during which time a total of 710 psi of acetylene was absorbed. Steam distillation of the mixture was continued until 2 l. of distillate had been collected; 23.0 g of cyclooctatetraene was isolated from this distillate. Sodium carbonate (18 g) and potassium hydroxide (5 g) were added to the distillation flask and the mixture was heated on a steam bath for 1 hr.[19] After filtration, the aqueous solution was made acidic and extracted with ten 100-ml portions of ether. The dried ether solution was evaporated at reduced pressure to yield a dark oil; addition of acetonitrile to this oil resulted in the formation of 3.46 g (10%) of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid as a yellow solid melting at 187–194° dec. Three recrystallizations from acetonitrile afforded material having mp 195–196° dec.

Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20; neut equiv, 96. Found: C, 62.22; H, 4.15; neut equiv, 93.

Dimethyl 2,4,6,8-Cyclooctatetraene-1,2-dicarboxylate. To a suspension of 161 mg of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid in 35 ml of ether, 10 ml of a 0.34 *M* ether solution of diazomethane was added. The solution was allowed to stand at 0° for 1 hr and at 25° for 1 hr. Acetic acid was added to decompose the excess diazomethane, the ether solution was extracted once with 10% sodium carbonate solution and dried with magnesium sulfate, and the solvent was removed at reduced pressure. Two recrystallizations of the residue from ligroin afforded 147 mg (80%) of the dimethyl ester having mp 108.0–109.2°.

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.72; H, 5.54.

Lithium Aluminum Hydride Reduction of Dimethyl 2,4,6,8-Cyclooctatetraene-1,2-dicarboxylate. A solution of 110 mg of dimethyl 2,4,6,8-cyclooctatetraene-1,2-dicarboxylate in 15 ml of dry ether was added dropwise over a period of 30 min to a mixture of 240 mg of lithium aluminum hydride and 30 ml of ether cooled in an ice bath. After the addition was complete, the reaction mixture was stirred for 6 hr at 0°, for 1 hr at 25°, and for 30 min at the reflux temperature. Water was added cautiously until a solid precipitate formed; this was collected on a filter and washed several times with acetone. The combined ether and acetone solutions were dried with magnesium sulfate, and the solvent was removed at reduced pressure. Distillation of the residue at 0.5-mm pressure afforded 41 mg (50%) of a yellow oil.

A 22-mg sample of the above oil in 0.3 ml of dry pyridine was treated with 0.08 ml of benzoyl chloride according to the procedure described above for the preparation of the dibenzoate. After five recrystallizations from ethanol–water, the white solid had mp 81.0–82.4°. A mixture of this substance and the dibenzoate of 1,2-di(hydroxymethyl)cyclooctatetraene prepared by the copolymerization reaction melted at 81.8–83.4°.

Monoquinine Salt of 2,4,6,8-Cyclooctatetraene-1,2-dicarboxylic Acid. A 222-mg sample of the dicarboxylic acid **4** in 25 ml of 95% ethanol was added to a solution of 551 mg of quinine hydrate in 20 ml of 95% ethanol. The solution was concentrated to approximately 5 ml and pentane was added. Cooling in a Dry Ice–acetone bath resulted in the crystallization of 514 mg (86%) of a pale yellow salt having mp 181.0–183.8° dec and $[\alpha]^{27}\mathrm{D}$ +94.2°

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(15) Melting points are corrected and boiling points uncorrected. Analyses were performed by Dr. S. M. Nagy and his associates.

(16) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

(17) A. Valette, *Ann. Chim.* (Paris), (12) **3**, 644 (1948).

(18) Cope and Campbell[2] report bp 99–105° (70 mm) and $n^{25}\mathrm{D}$ 1.4544–1.4559 for this material prepared by catalytic hydrogenation of 1,2-dimethylcyclooctatetraene, obtained from the copolymerization of acetylene and 2-butyne.

(19) This addition of base to the steam distillation residue and subsequent heating ensures complete saponification. The addition of sodium hydroxide or sodium carbonate to the reaction mixture prior to steam distillation resulted in foaming.

(c 1.0, 95% ethanol). After four recrystallizations from acetone the salt had mp 193.4° dec and $[\alpha]^{27}\mathrm{D}$ +99.5° (c 1.0, 95% ethanol).

Anal.[20] Calcd for $C_{30}H_{32}N_2O_6$: C, 69.75; H, 6.25; N, 5.42. Found: C, 69.52; H, 6.4; N, 5.52.

To a solution of 0.15 g of the monoquinine salt in 5 ml of 95% ethanol was added 8 ml of 3 N hydrochloric acid. The solution was diluted with 50 ml of water and extracted with five 15-ml portions of ether. The combined ether extracts were washed once with 4 ml of 2 N hydrochloric acid. The acidic solution was extracted once with ether, and the combined ether solutions were dried with sodium sulfate. The solvent was removed at reduced pressure, and the yellow solid residue was recrystallized three times from acetonitrile, yielding 12 mg of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid, mp 194.5° dec, $[\alpha]^{27}\mathrm{D}$ 0°.

Mono-*d*-α-methylphenethylamine (Dexedrine) Salt of 2,4,6,8-Cyclooctatetraene-1,2-dicarboxylic Acid. To 35 ml of a 10% sodium hydroxide solution was added 300 mg of Dexedrine sulfate. The mixture was shaken well and then extracted with three 25-ml portions of ether. After drying with calcium sulfate, the ether solution was filtered and concentrated to 50 ml. A 310-mg sample of 2,4,6,8-cyclooctatetraene-1,2-dicarboxylic acid in 2 ml of 95% ethanol was added to the ether solution. Upon heating, a pale yellow crystalline salt separated (477 mg, 91%) which after five recrystallizations from ethanol–ethyl acetate afforded 231 mg of the salt having mp 156.8–158.6° dec and $[\alpha]^{27}\mathrm{D}$ +4.7° (c 1.0, 95% ethanol).

Anal.[20] Calcd for $C_{19}H_{21}NO_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.89; H, 6.39; N, 4.52.

To a cold solution of 128 mg of the salt in 3 ml of methanol, 9 ml of a dilute hydrochloric acid solution (approximately 1.5 N) containing cracked ice was added. The solution was diluted to 40 ml with water and extracted with five 15-ml portions of ether. The combined ether solutions were extracted once with 5 ml of 3 N hydrochloric acid and dried with magnesium sulfate. Removal of the solvent at reduced pressure afforded 46 mg (61%) of the dibasic acid **4**, which after one recrystallization from acetonitrile had mp 195–197° dec and $[\alpha]^{27}\mathrm{D}$ 0°.

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[20] This analysis was obtained by combustion after mixture with copper oxide.

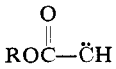
Cycloadditions. XII. The Relative Reactivity of Carbethoxycarbene and Carbethoxynitrene in Cycloadditions with Aromatics[1,2]

John E. Baldwin[3] and Roger A. Smith[4]

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received November 4, 1966*

Abstract: Carbethoxycarbene and carbethoxynitrene have been generated through the thermal decomposition of ethyl diazoacetate and ethyl azidoformate at 129.6° in a solution of benzene and anisole, toluene, chlorobenzene, fluorobenzene, or trifluoromethylbenzene in an unreactive perfluorinated polyether. From the relative rates at which the aromatic substrates were consumed in the competitive situation obtaining, linear free energy correlations of carbethoxycarbene and -nitrene reactivity were established. The Hammett ρ for the carbethoxycarbene additions to monosubstituted benzenes was −0.38; for the carbethoxynitrene additions, ρ was −1.32.

Carbenes[5,6] and nitrenes[7] are isoelectronic species which have been characterized or postulated as intermediates in various reactions. Carbon is divalent in carbenes, while nitrogen is monovalent in nitrenes; either may have two nonbonding electrons spin paired (singlet state) or spin unpaired (triplet state). In the singlet state, carbenes or nitrenes behave as electrophiles or nucleophiles, depending upon their complete structure. In the triplet state they may manifest radical character. Such diverse possibilities for chemical reactivity in a single family of species engender special theoretical and practical chemical interest.


$\mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-\ddot{C}H}$

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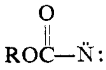
$\mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{-\ddot{N}:}$

2

Carbalkoxycarbenes **1** and carbalkoxynitrenes **2** are less reactive and more selective than unsubstituted carbene and nitrene in such characteristic reactions as insertions into aliphatic carbon–hydrogen bonds and additions to olefinic and aromatic carbon–carbon bonds.[8–11] They may also enter into 1,3 cycloadditions with reaction partners containing suitable multiple bonds,[12,13] processes inaccessible to simpler carbenes and nitrenes. Their structural similarities and capabilities of participating in at least four distinct types of intermolecular processes make possible a wide range of comparisons of relative reactivity and selectivity, which could lead to an unusually detailed knowledge of the chemical behavior of these comparatively unstable reactive intermediates.

Quantitative data on the relative reactivity of carb-

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[1] Paper XI in this series: J. E. Baldwin, M. C. McDaniel, M. G. Newton, and I. C. Paul, *Tetrahedron Letters*, 4239 (1966).

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[5] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[6] J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

[7] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[8] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

[9] K. C. Zahn, Abstracts, Organic Division Seminars, Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill., Spring 1966, p 113.

[10] W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

[11] J. E. Baldwin and R. A. Smith, *ibid.*, **87**, 4819 (1965).

[12] W. Lwowski, A. Hartenstein, C. deVita, and R. L. Smick, *Tetrahedron Letters*, 2497 (1964).

[13] R. Huisgen and L. Ghosez, *Chem. Ber.*, **97**, 2628 (1964); R. Huisgen and H. Blaschke, *Ann.*, **686**, 145 (1965).