Chemistry of Dianions. Formation and Reactivity of Some Anionic Species Derived from Tetraphenylbutatriene

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The reactions of tetraphenylbutatriene (I) with alkali metals have been examined. The resulting dianion was converted to 1,1,4,4-tetraphenylbutyne-1,4-dicarboxylic acid (IV) and the latter then decarboxylated to 1,1,4,-4-tetraphenyl-1,3-butadiene (V) in good yield. Protonation of the dianion has been shown to yield two new products: 1,1,4,4-tetraphenyl-1,2-butadiene and a new dimer, 1,2-bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane. The nature of the dianion formed from tetrakis(diphenylmethylene)cyclobutane and sodium has also been examined.

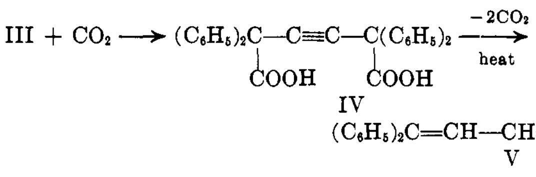
The reactions of tetraphenylbutatriene with alkali metals were being studied in our laboratory at the time Zweig and Hoffmann published a paper on similar work.[1] In general our data support the findings of these workers. The intermediate formation of II was indicated by its e.s.r. signal and the signal persisted for days when only 1 equiv. of alkali metal was used. Upon further treatment with alkali metal the signal disappeared indicating the formation of the dianion. We also observed the cleavage of 1,4-dimethoxy-1,1,4,4-tetraphenyl-2-butyne with potassium–sodium in dimethoxyethane to form first the cumulene (I) and finally the dianion (III). The reaction also takes place with either potassium or sodium alone.

$$\underset{\text{I}}{(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2} \xrightarrow[\text{THF or DME}]{\text{Na in}}$$

$$\underset{\text{II}}{(C_6H_5)_2\bar{C}{-}C{\equiv}C{-}C(C_6H_5)_2} \xrightarrow{\text{Na}}$$

$$\underset{\text{III}}{[(C_6H_5)_2C{-}C{\equiv}C{-}C(C_6H_5)_2]^{-2}\ 2Na^+}$$

Further work, in our study, showed that the dianion obtained from both tetraphenylbutatriene and 1,4-dimethoxy-1,1,4,4-tetraphenyl-2-butyne was converted in high yields to 1,1,4,4-tetraphenylbutyne-1,4-dicarboxylic acid (IV) by treatment with carbon dioxide. This appears to be an excellent method for preparing this acid. The dicarboxylic acid underwent decarboxylation on melting to form 1,1,4,4-tetraphenyl-1,3-butadiene (V). Compound V also formed an anion radical (VI) and a dianion (VII) when treated with alkali metals. 1,1,4,4-Tetraphenyl-2-butene-1,4-dicarboxylic acid (VIII) was formed when VII was treated with carbon dioxide. The solution of V after treatment with 1 equiv. of sodium gave a strong e.s.r. peak (21.4 gauss). After further stirring with sodium, the signal disappeared.



$$\text{III} + CO_2 \longrightarrow \underset{\text{IV}}{(C_6H_5)_2\underset{\text{COOH}}{\underset{|}{C}}{-}C{\equiv}C{-}\underset{\text{COOH}}{\underset{|}{C}}(C_6H_5)_2} \xrightarrow[\text{heat}]{-2CO_2} \underset{\text{V}}{(C_6H_5)_2C{=}CH{-}CH{=}C(C_6H_5)_2}$$

$$(C_6H_5)_2C{=}CH{-}CH{=}C(C_6H_5)_2 \xrightarrow[\text{THF or DME}]{\text{Na in}}$$

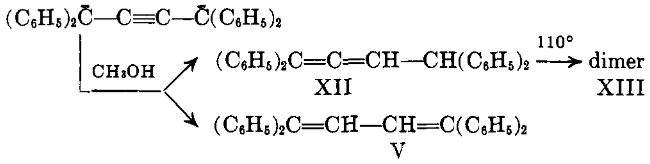
$$(C_6H_5)_2\bar{C}{-}CH{=}CH{-}\dot{C}(C_6H_5)_2 \xrightarrow{\text{Na}}$$

$$\underset{\text{VII}}{[(C_6H_5)_2C{-}CH{=}CH{-}C(C_6H_5)_2]^{-2}\ 2Na^+} \xrightarrow{CO_2} \text{VIII}$$

When the dianion III of tetraphenyl-2-butyne was treated with dimethyl sulfate and diethyl sulfate, respectively, good yields of the corresponding dialkylated products, 2,2,5,5-tetraphenyl-3-hexyne (IX) and 3,3,-6,6-tetraphenyl-4-octyne (X), were obtained. Treatment of the dianion VII of 1,1,4,4-tetraphenyl-1,3-butadiene with dimethyl sulfate gave 2,2,5,5-tetraphenyl-3-hexene (XI).

Protonation of III by treatment with methanol was reported by Bergmann to give two unidentified hydrocarbons, m.p. 97° and m.p. 167°.[2]

Table II in ref. 1 reports a 90% yield of 1,1,4,4-tetraphenyl-1,3-butadiene presumably from the protonation of III with methanol. There is no mention of the procedure used in the Experimental part of this paper. This reaction was found by us to give somewhat different results. The main product was 1,1,4,4-tetraphenyl-1,2-butadiene (XII) with smaller amounts of 1,1,4,4-tetraphenyl-1,3-butadiene. When XII was heated at 110°, it was converted to a dimer (XIII).



$$(C_6H_5)_2\bar{C}{-}C{\equiv}C{-}\bar{C}(C_6H_5)_2 \xrightarrow{CH_3OH} \begin{cases} \underset{\text{XII}}{(C_6H_5)_2C{=}C{=}CH{-}CH(C_6H_5)_2} \xrightarrow{110^\circ} \underset{\text{XIII}}{\text{dimer}} \\ \underset{\text{V}}{(C_6H_5)_2C{=}CH{-}CH{=}C(C_6H_5)_2} \end{cases}$$

Brand reported in 1910 that 1,1,4,4-tetraphenyl-2-butyne gave a prototropic rearrangement with bases to form 1,1,4,4-tetraphenyl-1,3-butadiene and possibly 1,1,4,4-tetraphenyl-1,2-butadiene, although the latter was not actually identified.[3] The relative amounts of XII and V which are formed depend on the temperature. XII is formed first and isomerizes at higher temperatures to V. This example of kinetic *vs.* thermodynamic protonation is being more thoroughly studied.

Compound XII was isolated as pale yellow crystals, m.p. 98°, which gave a deep yellowish green fluorescence when exposed to ultraviolet light. The structure of XII was evidenced by its analysis, infrared, ultraviolet, and n.m.r. spectra. The infrared spectrum had bands at 1940 and 1080 cm.$^{-1}$. Bellamy reports 1940 and 1060 cm.$^{-1}$ for the stretching vibration bands for —C=C=C—.[4] The spectrum also showed tertiary C–H absorption at 2955 and 2890 cm.$^{-1}$.

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[1] A. Zweig and A. K. Hoffmann, *J. Am. Chem. Soc.*, **84**, 3278 (1962).

[2] E. Bergmann, *Ber.*, **63B**, 2593 (1930).

[3] K. Brand, *Z. Electrochem.*, **16**, 669 (1910).

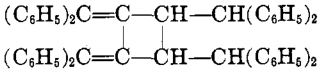
[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 58.

The ultraviolet spectrum showed no open-chain conjugation but showed the usual absorption for phenyl groups. The n.m.r. spectrum showed the following peaks: singlet, τ 2.9 (area ~20) for the phenyl groups; doublet, τ 3.9–4.0 (total area of doublet ~1) for the olefinic hydrogen (J = 15 c.p.s.); doublet, τ 5.1–5.2 (total area of doublet ~1) for the tertiary hydrogen (J = 15 c.p.s.). The two doublets are due to the fact that the two hydrogens are on adjacent carbon atoms and consequently split each other. 1,1,4,4-Tetraphenyl-1,2-butadiene (XII), found in the course of this work, probably is identical with the unidentified compound (m.p. 97°) reported by Bergmann.[2]

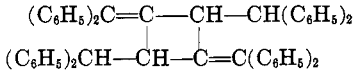
Catalytic hydrogenation of XII gave a quantitative yield of 1,1,4,4-tetraphenylbutane (XIV). Brand obtained the same compound (with same m.p. 121°) by hydrogenating 1,1,4,4-tetraphenyl-1,3-butadiene.[5] Further evidence for the structure of XIV was supplied by its n.m.r. spectrum.

When 1,1,4,4-tetraphenyl-1,2-butadiene was treated with sodium ethoxide in ethanol solution, a quantitative yield of 1,1,4,4-tetraphenyl-1,3-butadiene (V) was isolated. V was obtained as colorless needles, which gave a deep blue fluorescence when exposed to ultraviolet light. The ultraviolet spectrum of V gave strong evidence for its conjugated nature: $\lambda_{\max}^{C_2H_5OH}$ 340 mμ (ϵ 28,000), 249 (21,000), and 208 (42,000). The ultraviolet spectrum of V had previously been reported for its solution in hexane.[6] The two spectra are in good agreement. The m.p. 200° agrees with that reported by Kuhn and Fischer.[7] The n.m.r. spectrum for V also agreed with the assigned structure.

The structure of the dimer XIII has been shown to be 1,2-bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane on the basis of its analysis, molecular weight, and absorption spectra. Structure XV was also considered but it was eliminated by the data obtained. The n.m.r. spectrum gave the following information: τ 2.73 and 3.23 (total area ~40) for phenyl hydrogens; τ 5.75 and 5.90 (total area of doublet ~2) for α-H; τ 6.30 and 6.35 (total area of doublet ~2) for β-H. Either structure XIII or XV can explain the n.m.r. spectrum, but only XIII with its conjugated diene system can explain the ultraviolet: $\lambda_{\max}^{C_2H_5OH}$ 380 mμ (ϵ 7100), 320 (7800), and 260 (22,000).

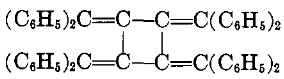


XIII



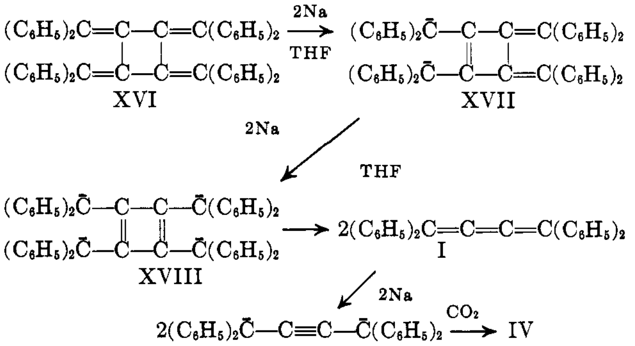
XV

In another paper, published during the course of the present study, the dimerization of tetraphenylbutatriene (I) was effected in the solid state by sunlamp irradiation.[8] The structure of this dimer (XVI) was proven to be tetrakis(diphenylmethylene)cyclobutane. This dimer was of special interest to us. Since it is comprised of two tetraphenyl-1,3-butadiene groups it would be expected to react easily with alkali metals. The expected result would be to force two double bonds into the ring to form an unstable cyclobutadiene derivative. When XVI was treated with sodium in tetrahydrofuran, under nitrogen, a purple solution was obtained. After pouring the solution over Dry Ice, a good yield of 1,1,4,4-tetraphenylbutyne-1,4-dicarboxylic acid (IV) was obtained. It was identical with the specimen prepared from I. The mechanism shown in Scheme I is proposed. The predicted instability of XVIII accounts for the cleavage to I. It is possible that it is the dianion XVII which cleaves rather than XVIII since the cyclobutyl ring in this intermediate is also destabilized.



XVI

SCHEME I



Another phase of anion chemistry was prompted by the report that disubstituted acetylenes when treated with sodium in liquid ammonia yield *trans* olefins through a *trans* ethylene dianion.[9] It occurred to us that if these dianions could be prepared in suitable solvents they would be useful intermediates for preparing disubstituted fumaric acids. For diphenylacetylene in tetrahydrofuran, the method worked rather well and diphenylfumaric acid was obtained. When 5-decyne was treated under similar conditions only cleavage products were identified. Cleavage is probably due to the instability of the dibutylethylene anion radical since the butyl groups do not offer so much resonance stabilization as do phenyl groups.

$$C_4H_9-\bar{C}=\underset{\cdot}{C}C_4H_9 \xrightarrow{K} C_4H_9K + C_4H_9C\equiv CK \xrightarrow[2.\ H^+]{1.\ CO_2} \underset{\text{valeric acid}}{C_4H_9COOH} + \underset{\text{2-heptynoic acid}}{C_4H_9C\equiv C-COOH}$$

Unless the intermediate anion radicals and dianions are stabilized by resonance as in the diphenyl derivative, the reaction is of no value for preparing disubstituted fumaric acids.

Experimental

Purification of Solvents and Acetylene.—Diethyl ether was dried by distilling ether from an ether solution of phenylmagnesium bromide. Tetrahydrofuran and 1,2-dimethoxyethane were stored in a 2-l. flask containing 1 mole of biphenyl–sodium solution from which these solvents were distilled as needed. Com-

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[5] K. Brand, *Ber.*, **54**, 2000 (1921).

[6] G. Kortum and G. Dreesen, *ibid.*, **84**, 182 (1951).

[7] R. Kuhn and H. Fischer, *ibid.*, **93**, 2285 (1960); Table II in ref. 1 gives m.p. 193–194°.

[8] R. O. Uhler, H. Schechter, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3397 (1962).

[9] K. N. Campbell and L. T. Eby, *ibid.*, **63**, 216, 2683 (1941); R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press Inc., New York, N. Y., 1955, p. 28.

mercial acetylene was passed through four traps containing dilute NaOH, concentrated H_2SO_4, P_2O_5, and KOH pellets, respectively.

Physical Data.—All melting points were determined in a Thomas-Hoover capillary melting point apparatus. All infrared spectra were obtained from KBr disks. A Perkin-Elmer Model 421 recording spectrophotometer was used. Ultraviolet spectra were obtained on a Beckman DU spectrophotometer equipped with an automatic recording attachment. N.m.r. measurements were made on a Varian n.m.r. spectrometer at 60 Mc. Electron p.m.r. spectra were obtained using a Varian EPRV-4500 spectrometer operating at 9000 Mc., with a magnetic field of 300 gauss and equipped with a 100-kc. field modulation.

Alkali Metal Adduct Solutions.—All adducts were prepared in a three-neck flask equipped with a mechanical stirrer. The alkali metal acceptor, the solvent, and the metal were introduced in a stream of nitrogen.

1,1,4,4-Tetraphenylbutatriene (I).—Compound I was prepared from 1,1,4,4-tetraphenylbutyne-1,4-diol.[10] Dupont used ethylmagnesium bromide, acetylene, and benzophenone as his reactants. We found the following procedure to give better results. Sodium (47 g., 2 g.-atoms) was stirred for 12 hr. under nitrogen with 2 l. of tetrahydrofuran and 320 g. (2.06 moles) of biphenyl. Acetylene was then bubbled into the blue solution until decolorization was complete. To the white slurry of sodium acetylide, 365 g. (2 moles) of powdered benzophenone was added, and the mixture was refluxed, with stirring, for 1 hr. After cooling, the contents of the flask were poured into a large excess of water. Petroleum ether (b.p. 66–75°) (500 ml.) was added, and the butynediol was removed by filtration. The product was washed with water, petroleum ether, and dried, yield 86%, m.p. 192° (lit.[10] m.p. 193°).

1,1,4,4-Tetraphenylbutyne-1,4-diol was converted to 1,1,4,4-tetraphenylbutatriene by the stannous chloride–hydrogen chloride method.[11] The product was recrystallized from xylene, yield 71%, m.p. 239° (lit.[11] m.p. 236°). The diol was also converted to the butatriene by the potassium iodide method,[12] yield 78%.

Tetraphenyl-2-butyne Dianion (III). A.—Tetraphenylbutatriene (20 g., 0.056 mole) was stirred with 5 g. of potassium in 700 ml. of tetrahydrofuran under nitrogen. The end of the reaction was indicated by the disappearance of the e.s.r. signal in *ca.* 8 hr. It was found that two atoms of potassium, sodium, or lithium reacted completely with 1 mole of tetraphenylbutatriene in the THF, DME, or diethyl ether in 8–15 hr.

B.—1,1,4,4-Tetraphenyl-1,4-dimethoxy-2-butyne (8.36 g., 0.02 mole) was stirred with 4 g. (0.1 g.-atom) of potassium and 1 g. of sodium in 200 ml. of dimethoxyethane for 24 hr., under nitrogen. The end of the reaction was indicated by the disappearance of the e.s.r. signal. It was found that four atoms of potassium reacted completely with 1 mole of the dimethoxy derivative.

1,1,4,4-Tetraphenylbutyne-1,4-dicarboxylic Acid (IV).—A solution of the dianion, as prepared in method A, was poured into a 4-l. beaker containing Dry Ice. The solvent was evaporated and the solid was extracted with water. The water solution was acidified with 5 *N* sulfuric acid and the precipitate was dissolved in ether and dried over anhydrous magnesium sulfate. The ether was removed, and the solid obtained was washed with carbon tetrachloride: yield 88%, m.p. 198° dec. (lit.[1] m.p. 194–195°), $\lambda_{\max}^{C_2H_5OH}$ 207 and 260 mμ ($\epsilon_{\max}$ 32,600 and 10,000). Comparable yields were obtained from the lithium salt also.

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.73; H, 4.93. Found: C, 80.56; H, 5.00.

1,1,4,4-Tetraphenyl-1,3-butadiene (V).—Ten grams of IV was heated just to the melting point until the evolution of carbon dioxide ceased (1–2 min.). After cooling, the solid was powdered and washed with acetone to give colorless V: yield 72%; m.p. 200°, lit.[13] m.p. 200° (ref. 1, Table II gives m.p. 193–194°); $\lambda_{\max}^{CH_3OH}$ 208, 249, and 340 mμ ($\epsilon_{\max}$ 42,000, 21,000, and 28,000). Kortum and Dreesen reported $\lambda_{\max}$ of 342 mμ for the conjugated diene absorption.[14]

1,1,4,4-Tetraphenyl-2-butene-1,4-dicarboxylic Acid (VIII) **from 1,1,4,4-Tetraphenyl-1,3-butadiene** (V).—Four grams of V (0.01 mole) was stirred with 2 g. of sodium in 200 ml. of DMF, in an atmosphere of nitrogen. The solution turned deep blue and after 15 min. gave a strong e.s.r. signal (21.4 gauss). After 15 hr. of stirring, the signal had disappeared, and the dianion was carboxylated by pouring the solution over powdered Dry Ice. The solvent was evaporated, and the residue was taken up in water. Acidification of the water solution gave a white precipitate which was removed, washed with a small amount of acetone, and dried: yield 60%, m.p. 230–232°.

Anal. Calcd. for $C_{30}H_{24}O_8$: C, 80.36; H, 5.36. Found: C, 80.51; H, 5.48.

Schlenk reported m.p. 262° for this diacid.[15] Ultraviolet absorption of the diacid occurred at 207 and 260 mμ thus ruling out a conjugated structure. Furthermore there was no absorption in the infrared in the region 1940–1965 cm.$^{-1}$ which eliminates an allene structure. The structure assigned to the diacid VIII therefore appears to be the correct one.

2,2,5,5-Tetraphenylhexyne (IX).—A solution of the dianion III was prepared from 1,1,4,4-tetraphenylbutatriene (I). A slight excess of dimethyl sulfate was added with stirring. After 30 min., 100 ml. of methanol was added to destroy the excess alkali metal. Evaporation of the solvent gave a white solid which was washed with dilute hydrochloric acid, then with methanol, and recrystallized from ether–benzene: yield 84%, m.p. 85°.[16]

Anal. Calcd. for $C_{30}H_{26}$: C, 93.26; H, 6.73. Found: C, 93.27; H, 6.83.

3,3,6,6-Tetraphenyl-4-octyne (X).—The procedure for IX was used here except diethyl sulfate was used in place of dimethyl sulfate; yield 88%, m.p. 131° (lit.[1] m.p. 128–129°).

Anal. Calcd. for $C_{32}H_{30}$: C, 92.75; H, 7.25. Found: C, 92.90; H, 7.28.

1,1,4,4-Tetraphenyl-1,2-butadiene (XII).—Tetraphenylbutatriene (3.56 g., 0.01 mole) was stirred under nitrogen with 1.5 g. (0.038 g.-atom) of potassium in 125 ml. of dry tetrahydrofuran for 24 hr. The reddish black solution was slowly added to 1 l. of methanol. The solution was neutralized with hydrochloric acid and evaporated to dryness. The residue was washed with water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and then evaporated. The residue was extracted with petroleum ether, leaving a residue. The residue was recrystallized from methanol to yield pure XII, yield 57%, m.p. 98°.[17]

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.14; mol. wt., 362. Found: C, 93.86; H, 6.06; mol. wt., 359.

The structure of XII was based on its infrared, ultraviolet, and n.m.r. spectra (see Discussion).

A residue from the methanol recrystallization of XII proved to be 1,1,4,4-tetraphenyl-1,3-butadiene (V), yield 20%, lit.[13] m.p. 200°, $\lambda_{\max}^{CH_3OH}$ 346 mμ (ε 28,000).

Hydrogenation of XII over platinum in benzene solution gave 1,1,4,4-tetraphenylbutane, m.p. 121° (lit.[5] m.p. 121°).

Isomerization of XII to V.—1,1,4,4-Tetraphenyl-1,2-butadiene (0.358 g.) was dissolved in 50 ml. of ethanol containing 1 g. of sodium ethoxide. The solution was refluxed for 3 hr. The solvent was removed, and the residue was washed with water, then dissolved in ether. After drying over anhydrous magnesium sulfate, the ether was removed to give 0.330 g. (92%) of 1,1,4,4-tetraphenyl-1,3-butadiene (V), m.p. 200°, $\lambda_{\max}^{CH_3OH}$ 346 mμ (ε 28,000).

1,2-Bis(diphenylmethylene)-3,4-bis(diphenylmethyl)cyclobutane (XIII).—The 1,2-diene XII (3 g.) was heated at 110° for 3 hr. After cooling, the solid was broken up and extracted with a small amount of petroleum ether. The residue melted at 273°, yield 25%.

Anal. Calcd. for $C_{56}H_{44}$: C, 93.86; H, 6.14; mol. wt., 716. Found: C, 94.06; H, 6.10; mol. wt., 720.

The ultraviolet and n.m.r. spectra for this compound are included in the discussion.

Reaction of Tetrakis(diphenylmethylene)cyclobutane (XVI) **with Sodium.**—Compound XVI was prepared by the method of Uhler, Shechter, and Tiers.[8] XVI (2 g.) was stirred under nitrogen with 0.46 g. of sodium in 150 ml. of DME. The solution was stirred for 24 hr. and then poured over excess Dry Ice. After

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[10] G. Dupont, *Ann. chim. phys.*, [8] **30**, 438 (1913).

[11] R. Kuhn and H. Krauch, *Ber.*, **88**, 309 (1955).

[12] J. Wolinsky, *Roczniki Chem.*, **29**, 23, 35 (1955); *Chem. Abstr.*, **50**, 3349 (1956); **52**, 10024 (1958).

[13] R. Kuhn and H. Fischer, *Ber.*, **93**, 2285 (1960).

[14] G. Kortum and G. Dreesen, *ibid.*, **84**, 182 (1951).

[15] W. Schlenk and E. Bergmann, *Ann.*, **463**, 98 (1928).

[16] M.p. 82.5–83.5° was reported by Zweig and Hoffmann.[1] These workers used methyl iodide as the methylating agent.

[17] This improved procedure is from the experimental work of Samuel Sisenwine, a graduate student at the University of Pennsylvania.

removing the solvent, the residue was taken up in water. The aqueous solution was acidified with 3 N sulfuric acid, and the resulting precipitate was dried and taken up in ether. The ether extract was dried over magnesium sulfate. Evaporation of the ether left 1.8 g. (72%) of 1,1,4,4-tetraphenylbutyne-1,4-dicarboxylic acid (IV), m.p. 198°. It was identical with IV in all respects.

Diphenylfumaric Acid.—Diphenylacetylene (1.78 g., 0.01 mole) was stirred, under nitrogen, with 1.2 g. of potassium in 100 ml. of THF. After 5 hr., the solution was poured over excess Dry Ice. Decolorization was immediate. The solution was evaporated and the residue was extracted with water. The aqueous layer was acidified to liberate the dicarboxylic acid which separated as a gummy solid. After several days the product crystallized. After thorough washing with carbon tetrachloride a 25% yield of diphenylfumaric acid was obtained, m.p. 266°,[18] neut. equiv. 134 (calcd. 134). The use of lithium in place of potassium gave slightly higher yields.

Reaction of 5-Decyne with Sodium-Potassium Alloy.—5-Decyne (10 g., 0.073 mole) in 250 ml. of DME was added to the alloy (4 g. of K to 0.5 g. of Na) under nitrogen, and the mixture was stirred for 10 hr. It was then poured over Dry Ice. The solvent was removed under reduced pressure, and the residue was extracted with water. The aqueous layer was acidified and extracted with ether. Evaporation of the ether gave 4.5 g. of oily product. Careful fractional distillation gave two fractions, 68–71° at 5 mm. and 108–111° at 5 mm. The lower boiling product proved to be valeric acid.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.82; H, 9.80; neut. equiv., 102. Found: C, 58.57; H, 9.98; neut. equiv., 101.

The higher fraction was shown to be 2-heptynoic acid.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.66; H, 7.94; neut. equiv., 126. Found: C, 66.57; H, 7.97; neut. equiv., 125.

Triple-bond absorption in the infrared occurred at 2240 cm.$^{-1}$, $\lambda_{max}^{C_2H_5OH}$ 207 mμ (ϵ 69,500).

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[18] S. Wawzonek and D. Wearring [*J. Am. Chem. Soc.*, **81**, 2067 (1959)] reported m.p. 263–265° for a sample prepared by a different method.

Ozonides from Asymmetrical Olefins. Reaction with Triphenylphosphine

OTTO LORENZ AND CARL R. PARKS[1]

Contribution No. 310, Research Laboratory, Goodyear Tire and Rubber Company, Akron, Ohio

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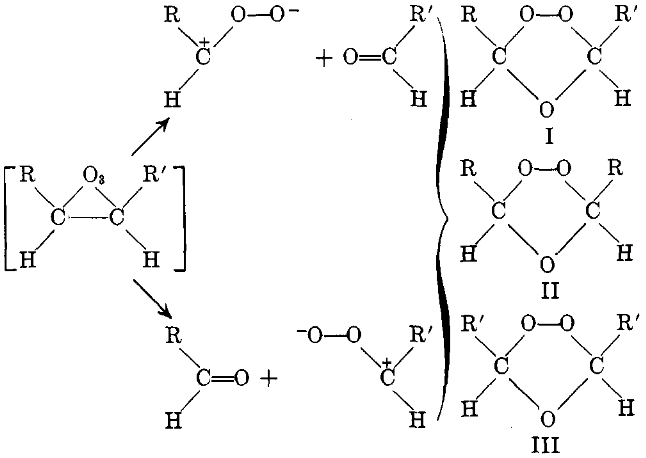
The ozonation of asymmetrical olefins, R—CH=CH—R′, has led to one asymmetrical or natural ozonide and two symmetrical or unnatural ozonides as predicted by the Criegee mechanism. The relative yields of the three ozonides were determined by gas chromatography. The investigation was carried out with 2-hexene, 4-methyl-2-pentene, 4-nonene, and 2,6-dimethyl-3-heptene at −78°. The ozonides were reduced quantitatively with triphenylphosphine to the corresponding carbonyl compounds. 2-Butene ozonide and 2,5-dimethyl-3-hexene ozonide could be separated into *cis* and *trans* isomers by g.l.c. technique. One of these isomers was more readily reducible by triphenylphosphine than the other which permitted the preparation of the less reactive isomer in pure form. The *cis–trans* ratio of the ozonides depended largely on the nature and steric configuration of the original olefin. This would indicate that some of the ozonides were formed by a stereospecific mechanism.

A previous investigation of the ozonation of 2,6-dimethyl-2,6-octadiene in the absence of a solvent showed that 2-butene ozonide was one of the reaction products.[2] To our knowledge this was the first reported example of the formation of an unnatural ozonide. This was considered as a further verification of the Criegee mechanism[3] since 2-butene ozonide was formed presumably by reaction of the zwitterion $H_3C—{}^+CH—O—O^-$ with acetaldehyde. Identification of other ozonides formed during the ozonation of 2,6-dimethyl-2,6-octadiene proved to be difficult since a variety of ozonides could be formed. It was decided, therefore, to investigate a number of simple asymmetrical olefins, R—CH=CHR′, which according to Criegee's mechanism may give rise to three different monomeric ozonides as shown below assuming a primary ozonide to be the initial product.[4] A necessary requirement for the formation of the natural ozonide I and the two symmetrical or unnatural ozonides II and III is a sufficient lifetime for the zwitterions to react statistically as well as the absence of a complete solvent cage which would prevent the formation of the unnatural ozonides. After our work had been completed, papers by Riezebos and co-workers[5] and Privett and Nickell[6] came to our attention in which it was shown that the ozonation of methyl oleate yielded the three possible ozonides.



The ozonation of four asymmetrical olefins, 2-hexene, 4-methyl-2-pentene, 4-nonene, and 2,6-dimethyl-3-heptene, as well as three symmetrical olefins, 2-butene, 3-hexene, and 2,5-dimethyl-3-hexene, was investigated. The ozonation was carried out at −78°, usually in a solvent such as n-pentane. The monomeric ozonides were separated from the total ozonation product, which usually contained much polymeric material, by distillation, and the yield was determined by weight. Gas chromatographic analysis showed that the symmetrical olefins formed only one ozonide, whereas the asymmetrical olefins gave three different

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[1] To whom communications should be sent.

[2] Presented before the Division of Rubber Chemistry, American Chemical Society, Cleveland, Ohio, Oct. 18, 1962; O. Lorenz and C. R. Parks, *Rubber Chem. Technol.*, **36**, 201 (1963).

[3] R. Criegee, *Ann.*, **583**, 1 (1953); R. Criegee, *et al.*, *Chem. Ber.*, **88**, 1878 (1955); for a summarizing discussion of ozonation, see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[4] R. Criegee and G. Schroeder, *Chem. Ber.*, **93**, 689 (1960).

[5] G. Riezebos, J. C. Grimmelikhuysen, and D. A. van Dorp, *Rec. trav. chim.*, **82**, 1234 (1963).

[6] O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).