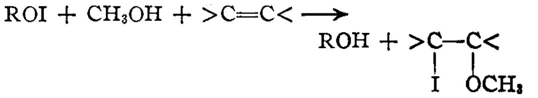
undergoes the following sequence of rapid reactions

$$ROI + H^+ \longrightarrow ROH + I^+ \qquad (1)$$
$$I^+ + I^- \longrightarrow I_2$$

Evidence for the existence of the intermediate hypoiodite was sought for by attempted reaction with cyclohexene in methanol


$$ROI + CH_3OH + {>}C{=}C{<} \longrightarrow ROH + {>}\underset{\textstyle I}{\underset{|}{C}}{-}\underset{\textstyle OCH_3}{\underset{|}{C}}{<} \qquad (2)$$

A solution of sodium iodide in methanol was added dropwise to a solution of cumene hydroperoxide and cyclohexene in methanol. Considerable iodine was liberated, indicating that reaction (1) was taking place. However, a small amount of material was isolated that contained iodine and methoxyl group which is presumptive evidence that a hypoiodite was formed in the reaction.

Experimental

The rate of iodine formation was followed with a Klett-Summerson photoelectric colorimeter, fitted with a Corning 5112 glass filter between the light source and the cell; a voltage stabilizer was utilized to supply the light source with a constant voltage. A series of standard iodine solutions were used to calibrate the colorimeter. The procedure was: 27 ml. of a buffered cumene hydroperoxide solution was placed in the absorption cell and a slow stream of nitrogen was passed through the solution for 15 minutes, then 3 ml. of a potassium iodide solution was added at zero time, the nitrogen sparge tube was removed, and the cell was capped to exclude air. The cell was maintained at 25 ± 0.1° in a constant-temperature bath, from which it was removed at periodic intervals to determine the optical density.

The cumene hydroperoxide used was of 96% purity and the hydroperoxide solutions were buffered with recrystallized monopotassium phosphate and carbonate-free 0.1 *N* sodium hydroxide.

Solutions of sodium oxalate, oxalic acid, potassium iodide, iodine and cumene hydroperoxide were made as shown in Table I for detecting free-radical intermediates according to Taube's method.[3] Oxygen was excluded from the solutions by flushing the flasks (regular iodine flasks) with nitrogen whenever they were opened. After the cumene hydroperoxide had reacted completely, 25-ml. samples were titrated periodically with 0.0102 *N* sodium thiosulfate to determine the rate of iodine consumption by the thermal reaction with oxalate ion.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE NATIONAL INSTITUTES OF HEALTH]

Crystalline Ozonides from *cis–trans*-Ethylene Derivatives[1]

BY SIDNEY M. GOODWIN, N. M. JOHNSON AND B. WITKOP

RECEIVED APRIL 13, 1953

Ozonolysis of the methyl, ethyl and phenyl esters of fumaric and maleic acids leads only to one type of crystalline ozonide presumably the (resolvable) *trans* structure (Ia, Ib, Ic).

Whereas fumaric acid is practically inert to the action of ozone,[2] ethyl fumarate yields a crystalline ozonide, m.p. 42–43°, in moderate yield,[3] the significant infrared bands of which are shown in Table I. The crystalline ozonide from diethyl *maleate* melted at 37–42°, gave no significant depression on admixture and showed an infrared spectrum (main bands, see Table I) identical with the ozonide from diethyl fumarate. This identity of the infrared spectra of the ozonides from diethyl as well as dimethyl maleate and fumarate has not been observed by Briner[4] because only solutions of ozonized compounds, but not the crystalline ozonides, were employed for the infrared measurements. As

TABLE I

INFRARED SPECTRA IN CHLOROFORM

Compound	Infrared absorption in chloroform Ester carbonyl	 >C=C< and phenyl	 C–O–C region[a]
Dimethyl fumarate	5.82	6.08	....
Dimethyl maleate	5.80	6.07	....
Diethyl fumarate	5.83	6.08	....
Diethyl maleate	5.79	6.08	....
Dimethyl $\left\{\begin{matrix}\text{fumarate}\\ \text{maleate}\end{matrix}\right\}$ ozonide	5.68	..	9.0-9.15^{b}; 10.0–10.2
Diethyl $\left\{\begin{matrix}\text{fumarate}\\ \text{maleate}\end{matrix}\right\}$ ozonide	5.68	..	9.08, 9.82, 10.08
Diphenyl fumarate	5.75	6.12, 6.26	9.37, 9.79
Diphenyl fumarate ozonide	5.60	6.27	9.08–9.15^{a}; 9.80 (w), 10.06–10.12^{b}
Diethyl diphenyl maleate	5.80^{s}	6.18^{w}	9.14^{w}; 9.24^{w}; 9.30^{m}; 9.49^{s}; 9.77^{s}
Diethyl diphenyl maleate	5.76	..	9.21^{s}; 9.84^{s}; 10.20

[a] *Cf.* O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951); G. M. Barrow and S. Searles, THIS JOURNAL, **75**, 1175 (1953). [b] In the region near 9μ, the rather broad band is at 9.125μ which corresponds with the value of Briner (1097 cm.$^{-1}$).[4] In the 10μ region a band at 10.08μ is found which in the ozonides from the methyl esters shifted to 10.18μ.

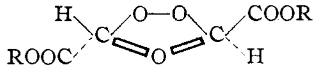
---

(1) Oxidation Mechanisms. XI. Preceding paper in this series: B. Witkop and S. Goodwin, THIS JOURNAL, **75**, 3371 (1953).

(2) C. D. Harris, *Ber.*, **65**, 1471 (1932).

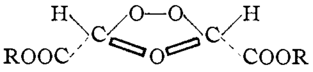
(3) R. Pummerer and H. Richtzenhain, *Ann.*, **529**, 53 (1937). The stable "ozonide" from dihydrodicyclopentadiene, m.p. 116–120°, [*cf.* H. Staudinger, *Ber.*, **58**, 1095 (1925)] mentioned subsequent to the description of the ozonolysis of diethyl fumarate, is no true ozonide, since it shows a strong carbonyl band at 5.76 μ.

(4) E. Dallwigk, B. Susz and E. Briner, *Helv. Chim. Acta*, **35**, 353 (1952).



I

trans form, theoretically resolvable



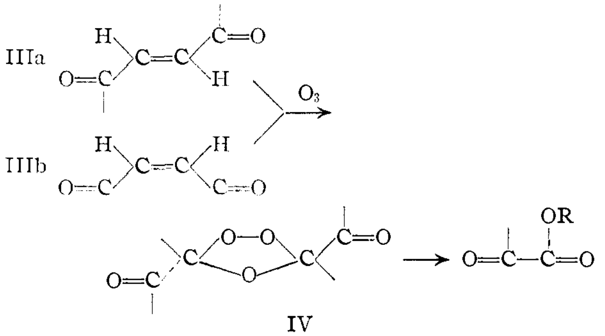
II

cis or *meso* form, not resolvable

Ia, R = CH_3, m.p. 23–27°
Ib, R = C_2H_5, m.p. 37–42°
Ic, R = C_6H_5, m.p. 108–110°

Criegee has pointed out independently,[5] isomeric ozonides such as I and II are not obtained in the maleate–fumarate series[6] but only one type of isomer, presumably the sterically and thermodynamically more favored *trans*-ozonide I. Dimethyl[7] (m.p. 95–97°) and diphenyl fumarate[8] (m.p. 162°, infrared spectrum Table I) gave two crystalline ozonides, Ia, m.p. 23–27°, undepressed on admixture with the ozonide from dimethyl maleate, and Ic, m.p. 108–110°, which was more stable than the aliphatic ester ozonides. Preliminary attempts to cleave this ozonide with triphenylmethyl radical[9] are reported in the Experimental section.

The infrared data in Table I show clearly the shift $(\sim 0.15\ \mu)$ to lower wave length in the absorption of the ester carbonyl when the conjugated system IIIa or IIIb is disrupted by formation of the ozonide (IV).



IV

On standing and decomposition the ozonide methyl and ethyl esters show a higher absorption in the carbonyl region (at 5.75 μ) identical with that of glyoxylic methyl and ethyl esters.

Diethyl diphenylmaleate[10,11] in solutions of ethanol, ether–cyclohexane and chloroform at 0° or −15° employing 50–200% excess of ozone led only to oily products.

The preparation of stable ozonides with suitable functional groups to facilitate resolution into optical antipodes will be investigated.

Experimental[12]

Diethyl Fumarate Ozonide (Ib).—The procedure of Pummerer and Richtzenhain[3] was followed. A solution of 6 g. of diethyl fumarate in 40 ml. of carbon tetrachloride was treated with ozone for two hours (300% excess). The solution was cooled by means of an ice–salt-bath during the addition of ozone. Fine, colorless needles crystallized near the end of the reaction period. After further standing in the cold, the crystalline solid was collected and washed with pentane. This material melts at 39–40°; yield 10–12%.

Diethyl Maleate Ozonide (Ib).—Diethyl maleate[13] upon treatment with ozone as described afforded a colorless crystalline ozonide melting at 37–42°. A mixture of the ozonides derived from diethyl fumarate and diethyl maleate melted at 36–38°.

Dimethyl Fumarate Ozonide (Ia).—A solution of 6 g. (0.042 mole) of methyl fumarate in 80 ml. of chloroform was treated with a stream of ozone while maintaining a cooling bath temperature of −30°. The rate of flow of ozone was 0.4 mmole per min. The treatment was terminated after 135 min. (29% excess) at which time a small amount of white solid had separated from the blue solution. About 200 ml. of pentane was added and the mixture was kept at −70°. The white crystalline solid (about 2 g.) was collected and washed with pentane in the cold room. The colorless microcrystalline prisms became sticky at 16° and melted at 23–27°. The ozonide gave a positive starch–iodide reaction and no gas evolution was observed on the addition of lead tetraacetate to a methanol solution of the compound.[14] A sample in a test-tube brought to room temperature gave a clear colorless melt which after a few minutes decomposed with the evolution of gas and considerable heat. A sample of the ozonide in a spoon did not decompose vigorously on being heated in a bunsen flame, whereas the ozonides in the ethyl ester series detonated under these conditions. The chloroform solution of the crystalline ozonides for the infrared measurements was made up in the cold room and the spectra were recorded without delay. An attempted combustion to obtain analytical figures caused a severe explosion.

Dimethyl Maleate Ozonide (Ia).—A solution of 6 g. of dimethyl maleate in 80 cc. of chloroform at −20° was treated with a stream of ozone for 231 min. (175% excess). The reaction mixture was cooled to −70° and diluted with 200 ml. of pentane. After one hour the lovely rosettes of colorless crystals were collected in the cold and washed with pentane. The melting point determined as described above was 18–23°. The melting point of a mixture of ozonides from dimethyl maleate and dimethyl fumarate was 21–24°.

Ozonization of Diethyl Diphenylmaleate. A.—A solution of 0.973 g. of diethyl diphenylmaleate in 30 cc. of ethanol was treated with ozone for 8.3 min. (50% excess). The temperature was kept at about 0°. On concentration of the reaction mixture *in vacuo* the starting material was recovered almost quantitatively.

B.—A solution of 0.5 g. of this ester in a mixture of 20 cc. of ether and 10 cc. of cyclohexane was treated with a large excess of ozone with cooling. Evaporation of the solvent afforded an oil. The infrared spectrum had the characteristic broad band in the 9 μ region and carbonyl absorption at 5.76 μ (starting material 5.81 μ).

C.—A solution of 3 g. of the ester in 60 cc. of chloroform at −15° was treated with a stream of ozone having a rate of flow of 0.34 mmole per min. until a 200% excess of ozone had been introduced. No crystalline material appeared even on dilution with pentane and cooling to −70°.

Ozonolysis of Maleic Anhydride.—A solution of maleic anhydride in chloroform was treated with a large excess of ozone at −15°. The solution was diluted with two volumes of pentane and the colorless solid which precipitated was collected in the cold room. A sample spontaneously decomposed on being transported to the instrument room.

Diphenyl Fumarate Ozonide (Ic).—A solution of 6.0 g. (22.4 mmoles) of diphenyl fumarate in 150 cc. of chloroform was cooled to −15° by means of an ice–salt-bath. Ozone was bubbled through the solution for 90 minutes (calculated time for one equivalent of ozone was 25 minutes).[15] The

---

(5) R. Criegee, 120th A.C.S. Meeting, New York, N. Y., September 7, 1951; Abstracts, p. 22M.

(6) G. Lohaus, Dissertation, Karlsruhe, 1952; quoted from R. Criegee, "Herstellung und Umwandlung von Peroxyden, in Methoden der Organischen Chemie (Houben-Weyl)," Vol. VIII, Part III, G. Thieme Verlag, Stuttgart, 1952, p. 30.

(7) C. A. Bischoff and A. v. Hedenström, *Ber.*, **35**, 4087 (1902).

(8) R. Anschütz and Q. Wirtz, *ibid.*, **18**, 1948 (1885).

(9) *Cf.* B. Witkop, J. B. Patrick and H. M. Kissman, *Ber.*, **85**, 949 (1952).

(10) Ramart-Lucas and J. Hoch, *Ann. chim.*, [10] **13**, 396 (1930).

(11) The attempt to prepare this compound by condensation of ethyl benzoylformate with ethyl phenylacetate using basic catalysts (*cf.* E. P. Kohler and B. B. Corson, THIS JOURNAL, **45**, 1975 (1923)) was not successful.

(12) All melting points are corrected.

(13) Kindly made available through the courtesy of Union Carbide and Carbon Co.

(14) R. Criegee, H. Pilz and M. Flygare, *Ber.*, **72**, 1799 (1939).

(15) In one experiment when the reaction time was twice as long, the white solid product decomposed vigorously a few minutes after being collected. Probably the benzene rings had been attacked by ozone.

white solid which appeared toward the end of the reaction time was collected and washed with pentane. Dilution of the mother liquor with an equal volume of pentane caused more precipitation. The combined solids (3.6 g., 51% yield) on recrystallization from benzene afforded long white needles melting at 108–110° (Kofler).

Anal. Calcd. for $C_{16}H_{12}O_7$: C, 60.76; H, 3.83. Found: C, 60.77; H, 3.94.

The reaction of a benzene solution of this ozonide with 2–4 moles of a solution of triphenylmethyl in benzene gave, after a varying short induction period, a bright red color which faded after standing for several minutes. From such mixtures could be isolated by fractionation with pentane or chromatographic absorption on alumina (1) unchanged ozonide, (2) triphenylmethyl carbinol, m.p. 162°, (3) triphenylmethyl peroxide, m.p. 186°, (4) in one instance a very small amount of colorless needles, m.p. 91–98°, possibly a molecular complex or mixture of the ozonide with hexaphenylethane: infrared spectrum: 5.60, carbonyl of the ozonide, 6.10^{s}, phenyl band present in triphenylmethyl derivatives.

BETHESDA 14, MD.

[Contribution from the Universal Oil Products Company]

The Mechanism of the Alkylation of Paraffins. III. The Reaction of Isobutane with 2-Chloro-4,4-dimethylpentane, 3-Chloro-5,5-dimethylhexane and 2- and 3-Chloro-3,4,4-trimethylpentane

By Louis Schmerling and J. P. West

Received May 6, 1953

The hydrogen–chlorine exchange reaction of 2-chloro-4,4-dimethylpentane with isobutane in the presence of aluminum chloride yielded 2,3- and 2,4-dimethylpentane in approximately equal amount. Similarly, skeletal rearrangement accompanying the reaction of 3-chloro-5,5-dimethylhexane with isobutane resulted in the formation of octane consisting of 34% 2,3- and 66% 2,4- and 2,5-dimethylhexane. The analogous reaction of 2- and 3-chloro-3,4,4-trimethylpentane yielded a mixture of trimethylpentanes (61% 2,2,4-, 28% of 2,3,4- and 11% 2,3,3-trimethylpentane). The significance of these results which may be considered as further evidence in support of the chain mechanism for the alkylation of isobutane with propene, 1-butene and 2-butene, respectively, is discussed.

In previous papers[1] in this series, evidence was described in support of a chain mechanism for the catalytic alkylation of isoparaffins with olefins. Further confirmation and an answer to an objection which has been raised are presented in the present communication.

Described in molecular (rather than ionic) terms the alkylation of isobutane with propene in the presence of aluminum chloride and hydrogen chloride involves the conversion of the isobutane to *t*-butyl chloride, the condensation of the *t*-butyl chloride with propene to yield 2-chloro-4,4-dimethylpentane and its isomerization products, 2- and 3-chloro-2,3-dimethylpentane. The chloroheptanes are subsequently converted to dimethylpentanes (an approximately equimolar mixture of 2,3- and 2,4-dimethylpentane) by chlorine–hydrogen exchange with isobutane which is thereby converted to *t*-butyl chloride and a new cycle is started. Miller[2] has pointed out that no chloro-2,4-dimethylpentanes were found in the product of the condensation of *t*-butyl chloride with propene in the presence of aluminum chloride although 2,4-dimethylpentane is a product of the aluminum chloride catalyzed alkylation of isobutane with propene.[3] That this observation (which had also been made in these laboratories) is not at variance with the proposed mechanism was shown by determining the products of the reaction of 2-chloro-4,4-dimethylpentane with isobutane in the presence of aluminum chloride at −35 to −7°. Hydrogen–chlorine exchange[4] occurred yielding heptanes and *t*-butyl chloride. The product formed by the reaction of 0.16 mole of the chloroheptane with excess isobutane consisted of 0.003 mole of pentane, 0.083 mole of *t*-butyl chloride, 0.053 mole of 2,4-dimethylpentane, 0.052 mole of 2,3-dimethylpentane and a minor amount of higher boiling material (Table I). There was no evidence of the presence of 2,2-dimethylpentane. It is obvious that the 2-chloro-4,4-dimethylpentane undergoes complete rearrangement during the chlorine–hydrogen exchange and that formation of 2,4-dimethylpentane occurs under alkylation conditions. The isolation of only 0.083 mole of *t*-butyl chloride per 0.105 mole of dimethylpentane was presumably due to interaction of the chloride with the catalyst to form lower layer complex.

The same complex reaction intermediate, $(CH_3)_3CCH_2CHCH_3^+(AlCl_4)^-$, is presumably involved as primary intermediate in the formation of 2,3- and 2,4-dimethylpentane by the reaction of isobutane with 2-chloro-4,4-dimethylpentane, and in the formation of 2-chloro-4,4-dimethylpentane and 2- and 3-chloro-2,3-dimethylpentane by the addition of *t*-butyl chloride to propene. The difference in skeletal structures of the products of the two reactions is due to a difference in the ease of the final step in each case.

Heptane is formed by the abstraction of a hydride ion from isobutane by a heptyl cation. Since this reaction occurs most readily with *t*-carbonium ions (II, IV and V), the heptane consists of 2,3- and 2,4-dimethylpentane mixed with little 2,2-dimethylpentane.

The chloroheptane is formed in part by dissociation of the complex, $C_7H_{15}^+AlCl_4^-$, but chiefly by the abstraction of a chloride ion from *t*-butyl chloride by a carbonium ion.[5] These are compara-

---

[1] (a) L. Schmerling, This Journal, **66**, 1422 (1944); (b) **67**, 1778 (1945); (c) **68**, 275 (1946).

[2] V. A. Miller, *ibid.*, **69**, 1764 (1947).

[3] (a) H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **64**, 33 (1942); (b) L. Schmerling, *ibid.*, **68**, 275 (1946).

[4] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1534 (1944).

[5] *Cf.* L. Schmerling and J. P. West, *ibid.*, **74**, 3592 (1952).