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CYCLOPROPENES FROM CARBENES AND ACETYLENES

STEREO-SELECTIVITY IN THE REACTION OF CARBOMETHOXYCARBENE WITH *CIS*-BUTENE

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Abstract—The addition of methylene and carbomethoxycarbene (generated photolytically from diazomethane and methyl diazoacetate, respectively) to butyne-2 gives 1,2-dimethylcyclopropene and methyl 1,2-dimethylcyclopropene-3-carboxylate, respectively. In identifying the hydrogenation product of the latter as *cis*-1,2-dimethylcyclopropane-3(*cis*)-carboxylate, it was relevant to investigate the reaction of *cis*- and *trans*-butene with methyl diazoacetate. It could be shown that addition was by the *cis*-mode, and that addition to *cis*-butene preferentially followed the sterically favored "exo" path.

CARBENES and acetylenes reacting to yield cyclopropenes is one of the many satisfying outgrowths of the renaissance of divalent carbon. Among the published examples, the earliest, by D'yakanov and Komendantov,[1] involves the reaction of phenylmethylacetylene with ethyl diazoacetate to give ethyl 1-methyl-2-phenylcyclopropene-3-carboxylate, while those immediately following, by Breslow *et al.*[2], involve the reactions of diphenylacetylene with diazomalonic ester,[2a,c] diazoacetic ester,[2b,c] phenyldiazoacetonitrile,[2d,e] and phenyl chlorocarbene.[2f] Quite recently, Vol'pin *et al.*[3] have reported the addition of dibromocarbene to diphenylacetylene, all the more significant an observation in view of the implication[4] that acetylenes should not be sufficiently nucleophilic to react. In this paper, we report the reactions of butyne-2 with two carbenes, methylene and carbomethoxymethylene, as the first illustrations of the synthesis of purely aliphatic cyclopropenes.

The decomposition of diazomethane is carried out photochemically in the usual way[5] with the exception that some dimethyl ether is admixed with the butyne-2 to prevent this relatively high melting substance from solidifying on the cold finger. Most of the unreacted butyne-2 is removed by distillation to give a concentrate from which quite unexceptional g.l.p.c. permits separation of dimethylcyclopropene in yields up to 17 per cent of theory based on N-nitrosomethylurea. Dimethylcyclopropene can be kept without polymerization in the refrigerator and in this sense is much more stable than unsubstituted cyclopropene which cannot be stored even at −75°.[6]

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[1] I. A. D'yakanov and M. I. Komendantov, *Vestnik Leningrad. Univ.* **11**, No. 22, *Ser. Fiz. i Khim.* No. 4, 166 (1956); *Chem. Abstr.* **52**, 2762[i] (1958).

[2a] R. Breslow and R. Winter, Abstracts of Papers presented at the 132nd Meeting of the Amer. Chem. Soc. p. 18P, New York, September, 1957; [b] R. Breslow and M. Battiste, *Chem. & Ind.* 1143 (1958); [c] R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.* **24**, 415 (1959); [d] R. Breslow, *J. Amer. Chem. Soc.* **79**, 5318 (1957); [e] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.* **80**, 5991 (1958); [f] R. Breslow, private communication.

[3] M. E. Vol'pin, Yu. D. Koreshkov and D. N. Kursanov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 560 (1959); *Chem. Abstr.* **53**, 21799[f] (1959).

[4] W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.* **80**, 5274 (1958).

[5] See, for example, W. von E. Doering and H. Prinzbach, *Tetrahedron* **6**, 24 (1959).

[6] M. J. Schlatter, *J. Amer. Chem. Soc.* **63**, 1733 (1941).

Support for the structure of 1,2-dimethylcyclopropene rests on the results of catalytic hydrogenation and on the interpretation of the n.m.r. spectrum. *cis*-1,2-Dimethylcyclopropane is obtained in good yield as the major product of reaction with one molar equivalent of hydrogen.[7] The minor products are n- and isopentane, easily separated in about equal amount by g.l.p.c. The n.m.r. spectrum of the olefin shows two absorptions at 198 and 245 cps in the approximate ratio, 3 : 1. Of the three possible structural isomers which could lead to 1,2-dimethylcyclopropane on hydrogenation, 1,2-dimethylcyclopropene alone would show methyl and cyclopropyl but no vinyl hydrogen in its n.m.r. spectrum. The mass spectrum confirms the molecular weight by having no mass numbers higher than 68. The most intense peak has the mass number, 67, of the parent minus one and may correspond to the 1,2-dimethylcyclopropenium ion, formed in greatest abundance by virtue of its special aromatic character.

In the infrared spectrum of 1,2-dimethylcyclopropene, the absence of any band in the 11·2 μ region where methylenecyclopropane absorbs strongly[8] is further evidence against an exocyclic methylene group. The weak absorption at 5·27 μ (CCl_4) is a point of obvious interest in the light of the anticipation by Faure and Smith[9] that the carbon–carbon double bond stretching frequency of cyclopropene should lie between those of simple olefins and acetylenes and of their actual finding that sterculic acid has a weak absorption at 5·35 μ (CS_2). There is no absorption in the ultraviolet.

The reaction of butyne-2 and methyl diazoacetate in the presence of light leads to methyl 1,2-dimethylcyclopropene-3-carboxylate (Chart 1, A). This molecule shows no absorption in the ultraviolet, has the required elementary analysis and an infrared spectrum which, lacking strong absorption at 3·23 and 11·2 μ, precludes the presence of exocyclic methylene. Catalytic hydrogenation affords a dihydro-derivative to which the structure, methyl *cis*-1,2-dimethyl-3(*cis*)-carboxylate (Chart 1, α), is assigned in the sequel.

The same α-ester is the minor product of both the photochemical and copper-catalyzed reactions of *cis*-butene with methyl diazoacetate; the major product (5 : 2) is methyl *cis*-1,2-dimethylcyclopropane-3(*trans*)-carboxylate (Chart 1, β). *trans*-Butene leads exclusively to a third product, methyl *trans*-1,2-dimethylcyclopropane-3-carboxylate (Chart 1, γ).

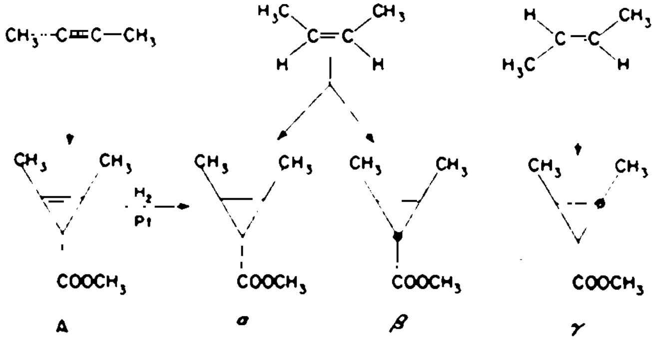

Chart 1. Reactions of methyl diazoacetate.

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[7] The infrared spectrum of this material is identical with that of the sample previously considered to be *cis*-1, 2-dimethylcyclopropane: W. von E. Doering and P. LaFlamme, *J. Amer. Chem. Soc.* **78**, 5447 (1956).

[8] J. T. Gragson, R. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Amer. Chem. Soc.* **75**, 3344 (1953).

[9] P. K. Faure and J. C. Smith, *J. Chem. Soc.* 1818 (1956).

On the assumption of stereospecific addition (logically, it is irrelevant whether *cis* or *trans*), of *cis* and *trans*-butene, one will give two stereoisomeric products and the other only one. This latter product, formed either by *trans*-addition to *cis*-butene or *cis*-addition to *trans*-butene, must have the *trans*-structure. In fact, the *single* product is obtained from *trans*-butene and is therefore methyl *trans*-1,2-dimethylcyclopropane-3-carboxylate (Chart I,γ). It follows that the mode of addition to the olefin must have been *cis*. Further justification for the assumption of stereospecific addition is to be found in the fact that there is no overlapping of products from *cis* and *trans*-butene—the former giving the *two* (and therefore *cis*) 1,2-dimethylcyclopropane-3-carboxylates, α and β, the latter the *single*, *trans* isomer, γ.[10]

INFRARED SPECTRA IN CARBON TETRACHLORIDE

A[a]		α[b]		β[c]		γ[d]	
μ	ε_r	μ	ε_r	μ	ε_r	μ	ε_r
3·36	10	3·38	10	3·40	10	3·39	10
5·71	55	5·74	60	5·75	80	5·74	55
6·77	10	6·82	9	6·83	15		
6·89	35	6·92	30	6·92	35	6·91	25
7·11	20	7·16	15	7·18	8	7·20	10
7·23	30	7·26	25	7·26	8	7·33	25
				7·56	35	7·68	15
				7·89	15	7·88	7
				8·13	15		
8·33	30	8·37	30	8·36	35	8·37	35
				8·50	60	8·49	50
8·59	90	8·63	95			8·58	50
8·94	90	8·97	8	8·86	10		
9·12	20	9·15	20	9·19	15	9·11	10
				9·42	6	9·44	10
9·72	8	9·75	6	9·60	8	9·72	6
				10·20	1	10·34	4
10·58	3			10·55	3	10·61	4
10·89	4	10·68	1	10·77	8	10·82	7
		11·06	2				
11·73	8	11·75	7			11·65	5
						12·13	8
14·08	8	14·12	7	14·18	7	14·71	3

[a] Methyl 1,2-dimethylcyclopropene-3-carboxylate. [b] Methyl *cis*-1,2-dimethylcyclopropane-3(*cis*)-carboxylate. [c] Methyl *cis*-1,2-dimethylcyclopropane-3(*trans*)-carboxylate. [d] Methyl *trans*-1,2-dimethylcyclopropane-3-carboxylate.

Structural distinction between the α and β *cis*-esters can be made by uncomplicated application of the principle of surface hindrance in catalytic hydrogenation.[11]

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[10] It is presumably by some such argument as this that the following, otherwise undocumented statements by P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.* **78**, 4496 (1956) find partial justification: "The criterion of stereospecific addition to the 2-butenes has been used to detect other carbene reaction intermediates. For example, photolyses of ethyl diazoacetate in the presence of these olefins produces carbethoxycarbene, $:CHCOOC_2H_5$, since the ethyl 2,3-dimethylcyclopropane carboxylates are obtained in stereospecific reactions. Copper-bronze catalysis produces the same results as photolysis."

[11] R. P. Linstead, W. von E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *J. Amer. Chem. Soc.* **64**, 1985 (1942).

Addition of hydrogen being from the catalyst surface to the under side of the absorbed olefin in *cis* fashion, the geometry of adsorption controls the stereochemistry of the product. In the case of methyl 1,2-dimethylcyclopropene-3-carboxylate, the favored conformation of adsorption leaves the methyl carboxylate group *trans* to the catalyst surface and leads to an all-*cis* product. Accordingly, the α-isomer is the methyl *cis*-1,2-dimethylcyclopropane-3(*cis*)-carboxylate and, by default, the β-isomer is the methyl *cis*-1,2-dimethylcyclopropane-3(*trans*)-carboxylate.

Parenthetically, it is noteworthy that the addition of carbomethoxy carbene to *cis*-butene is the only example in which, with *cis*-addition demonstrated, a second stereochemical choice, analogous to the *endo-exo* choice in the Diels–Alder reaction, is open to the reactants. Whereas the *endo* choice is overwhelmingly preferred in all but a few examples of the Diels–Alder, in the addition of this carbene no striking discrimination is shown. What little there is seems to be sterically controlled and corresponds in the Diels–Alder analogy to *exo*-addition. With *cis*-addition being indicated, the examples of Wilberg *et al.*[12] in which the additions of carboethoxycarbene to ethyl acrylate, vinyl bromide and vinyl *t*-butyl ether give *trans*-products, now become further illustrations of the steric favoring of *exo*-addition.

We hope to exploit the more ready availability of simple cyclopropenes by studying the chemistry of the ring system in greater detail than has heretofore been conveniently possible.

EXPERIMENTAL

1,2-*Dimethylcyclopropene*

A solution of diazomethane in decalin was prepared by adding 4·8 g N-methyl-N-nitrosourea to a well-stirred, ice-cold mixture of 40 ml decalin and 30 ml 45% aqueous potassium hydroxide over a period of 10 min. One quarter of the solution of diazomethane in decalin (at −70°) was transferred to a test-tube which was connected through a cork stopper and T-tube to two stopcocks: one leading to the top of the irradiation vessel—a simple, transparent Dewar-type of cold finger with an elongated outer wall, the inner wall serving as a dry-ice condenser—and a 1 l. reservoir; the other, to a vacuum pump. The diazomethane was transferred to the chilled (−70°) solution of 18 ml butyne-2 and 5 ml dimethyl ether in the Dewar vessel by evacuating the 1-l. bulb and allowing the decalin solution to warm to room temp. During irradiation, the upper part of the Dewar flask is protected by a jacket of aluminum foil and illumination is from below by two 275 watt General Electric Sunlamps. A total of eight doses of diazomethane was introduced at intervals sufficiently long to permit the decomposition of the preceding dose.

The reaction product was distilled, material boiling below 45° being collected. Analysis of the mixture by g.l.p.c. using a 2-m tetraisobutylene column (D) in a Perkin–Elmer 154 Fractometer operated at 26° and with helium at 10 lb/in^2 indicated 7·5% of the 1,2-dimethylcyclopropene corresponding to 17% of theory based on N-methyl-N-nitrosourea. On this column the retention time of butyne-2 is 10 min and that of dimethylcyclopropene is 16 min. Larger quantities of product were separated by distilling most of the butyne-2 in an 18″ helix-packed column and then passing many 100 mg samples of the concentrate through the 1/4″ g.l.p.c. column. Collection was accomplished in the usual manner in a U-tube surrounded by dry-ice. It was also possible to effect purification (>90%) on a 4′ g.l.p.c. column, 2″ in diameter, packed with didecylphthalate on firebrick.

1,2-Dimethylcyclopropene is a colorless, moderately stable liquid of f.p. −35 to −33° and having a vapor pressure of 150 mm at 0° (corresponding to a b.p. of about 40°). It polymerizes slowly at room temp and is easily stored at 4°. There is no maximum absorption in the U.V. above 215 mμ nor any absorption with log ε > 1 above 230 mμ (10^{-3} M solution in ethanol). The n.m.r. spectrum measured in a Varian Associates Model 4300 V at 40·01 mc with superstabilizer and spinning sample, showed two peaks, one at 198 ± 3, the other at 245 ± 3 c.p.s. (relative to the phenyl hydrogen of toluene) in an approximate ratio of 3:1. The gas-phase (10 mm pressure in an 8·5 cm cell) infrared

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[12] K. B. Wiberg, R. K. Barnes and J. Albin, *J. Amer. Chem. Soc.* **79**, 4994 (1957); E. N. Trachtenberg and G. Odion, *Ibid.* **80**, 4015 (1958); G. L. Closs and L. E. Closs, *Ibid.* **81**, 4996 (1959).

is comparatively simple. Omitting several very weak transitions, the spectrum seems to consist of the following bands: sharply separated, strong doublet at 3·43 and 3·52 μ; a weak peak at 5·27; weak peak at 6·70, moderate peak at 6·91, a poorly resolved doublet at 8·42 and 8·50 and a strong triplet at 9·78, 9·86 and 9·95 μ, with the central peak being exceedingly sharp. The spectrum in carbon tetrachloride (5%) follows: 3·44 (S); 3·52 (S); 5·29 (W); 5·81 (VW); 5·92 (VW); 6·75 (M); 6·93 (S); 8·46 (M); 8·63 (M); 9·91 (S).

The molecular weight was established by the mass spectral cracking pattern which shows no masses above the parent 68 (with the exception of the ^{13}C isotope mass at 69). The mass spectrum at 70 V. is given here along with intensities relative to that of mass 67 as 100: 69 (5·0), 68 (92·6) 67 (100·0), 66 (10·5), 65 (15·1), 63 (5·0), 62 (4·4), 61 (3·4), 60 (0·7), 54 (3·2), 53 (63·1), 52 (7·8), 51 (16·7), 50 (11·7), 49 (2·5), 44 (CO_2, 1·2), 43 (1·1), 42 (14·6), 41 (75·6), 40 (31·2), 39 (57·6), 38 (9·5), 37 (5·2), 36 (0·5), 32 (O_2, 1·4), 31·5 (1·4), 31 (6·1), 29 (3·2), 28 (N_2, 5·1), 27 (49·3), 26 (5·1), 25 (0·5), 15 (2·2).

Catalytic hydrogenation of 1,2-*dimethylcyclopropene*

In a vacuum-line system about 30 mg (20 cm mercury in the system employed) dimethylcyclopropene was condensed into 0·25 ml iso-octane containing 5 mg pre-reduced platinum oxide catalyst. Under 500 mm press of hydrogen, the cyclopropene was reduced at about 0° with magnetic stirring. Diffusion of the cyclopropene throughout the vacuum system was minimized by the appropriate use of stopcocks and by condensing the volatile materials back into the iso-octane solution by periodic cooling with dry-ice.

After uptake of hydrogen had ceased (a fall in pressure of 21 cm mercury), the hydrogenation product was condensed and chromatographed on a 2 m dioctylphthalate column at 25–26° with helium at 10 lb/in².

The most abundant product amounted to 70% of the volatile materials, and had the same retention time (about 16 min), mass spectrum and infrared spectrum as that of a sample of authentic *cis*-1,2-dimethylcyclopropane.[7]

The rest of the product consisted of two substances in roughly equal quantity having retention times of 10 and 7·5 min and being identified by mass spectroscopy as n-pentane and isopentane, respectively.

Methyl 1,2-*dimethylcyclopropene*-3-*carboxylate*

A mixture of 23 g butyne-2, 7 g methyl diazoacetate and 25 g isobutane (used as solvent to prevent the butyne-2 from crystallizing on the cold finger) was placed in a flask fitted with a condenser of the cold finger type filled with dry ice. At the end of 30 hr irradiation with three 275 watt General Electric sunlamps, the diazoacetic ester was decomposed. Distillation afforded 3·5 g material, b.p. 45–60° at 2 mm. Separation by g.l.p.c. (Perkin Elmer Fractometer 154; 4 m didecylphthalate column at 130°) afforded pure methyl 1,2-dimethylcyclopropene-3-carboxylate as the major component (80%) in 32% of theoretical yield; n_D^{20} 1·4412 (Found: C, 66·4; H, 8·2. $C_7H_{10}O_2$ requires: C, 66·7; H, 8·0%).

Catalytic hydrogenation of methyl 1,2-*dimethylcyclopropene*-3-*carboxylate*

The crude (80%) reaction product (0·5 g) was hydrogenated over platinum oxide in ethyl acetate at room temp and atm. press. The crude product was analysed by g.l.p.c. (4-m didecylphthalate column at 125° and helium at 25 lb/in²). At least 70% of the product had the same retention time and same infrared spectrum as the α-isomer, methyl *cis*-1,2-dimethylcyclopropane-3(*cis*)-carboxylate, obtained below from *cis*-butene and methyl diazoacetate. There was no detectable amount of any other stereoisomer.

Photochemical reaction of methyl diazoacetate with cis-*butene*

After being irradiated for 40 hr with three 275-watt General Electric sunlamps, a solution of 8 g methyl diazoacetate in 40 ml *cis*-butene had become colorless. Distillation afforded 4·0 g (39% of theory) material, b.p. 50–60° at 50 mm. In g.l.p.c. on a 4-m didecylphthalate column at 130° and 25 lb/in² of helium, the product consisted of a mixture mainly of two substances, α (r.t. 42 min; n_D^{20} 1·4308. Found: C, 65·5; H, 9·5. $C_7H_{12}O_2$ requires: C, 65·6; H, 9·4%) and β (r.t. 47 min; n_D^{20} 1·4306. Found: C, 65·5, H, 9·7. $C_7H_{12}O_2$ requires: C, 65·6; H, 9·4%) with small quantities of at least four other substances of shorter retention time. The ratio of α to β was about 2:5. Both isomers were stable to neutral permanganate solution.

The α-isomer was not rearranged appreciably to the β by treating with methanolic sodium methoxide for 6 hr at 60°.

The copper catalyzed reaction of methyl diazoacetate with cis-*butene*

This reaction was effected by adding gradually, at such a rate as to maintain a steady evolution of nitrogen, 3·0 g methyl diazoacetate and 2·5 g anhydrous copper sulfate to 20 ml *cis*-butene. Filtered and freed of volatile material, the product consisted largely of crystalline dimethyl fumarate with a small amount (5–10%) of the same mixture (2:5) of isomers α and β as above.

Photochemical reaction of methyl diazoacetate with trans-*butene*

In the same manner as above, 8·0 g methyl diazoacetate was irradiated in 50 ml *trans*-butene. Distillation afforded 3·5 g (34% of theory) material; b.p. 40–50° at 20 mm; n_D^{20} 1·4252. The major product, methyl *trans*-1,2-dimethylcyclopropane-3-carboxylate (Found: C, 65·3; H, 9·3. $C_7H_{12}O_2$ requires: C, 65·6; H, 9·4%), had a retention time of 33 min at 126° and at a helium pressure of 25 lb/in² in the same column as that used in the *cis*-butene experiment.

Infrared spectra

The spectra were measured in carbon tetrachloride solution in a 0·01 cm cell in a Perkin-Elmer Model 21 Infrared Spectrometer. Included in the tabulation of the spectra is a rough measure of intensity obtained from the optical densities by dividing by the product of the cell thickness (0·01 cm) and the concentration expressed in moles per 1000 g of carbon tetrachloride. The resulting "extinction coefficients" were normalized (ϵ_r) by taking the value 10 for the carbon–hydrogen stretching band.