

The ultraviolet spectrum of the *trans*-acid showed absorption maxima at 232 (ϵ 14,200), 278 (ϵ 1700), 283 (ϵ 1650) and 288 $m\mu$ (ϵ 1170) in 95% ethanol.⁴¹

DL-*cis*-9,10-Methyleneoctadecanoic Acid (Dihydrostercularic Acid).—A mixture of 22.0 g. (0.30 mole of zinc) of zinc-copper couple, 5.0 g. (0.02 mole) of iodine, 53.6 g. (0.20 mole) of methylene iodide, 29.6 g. (0.10 mole) of distilled methyl oleate (b.p. 128–132° (0.4 mm.), n_D^{25} 1.4506) and 100 ml. of anhydrous ether was stirred under reflux for 48 hours. The cool reaction mixture was filtered, and the filtrate was washed successively with 5% hydrochloric acid, water, and 5% sodium sulfite solution. After the solution had been dried over anhydrous magnesium sulfate, the ether was evaporated, and the residue was distilled to give 7.95 g. of recovered methyl oleate, b.p. 132–134° (0.4 mm.), n_D^{25} 1.4506. The distillation residue (17 g.) was heated under reflux with 4.0 g. of potassium hydroxide in 75 ml. of ethanol for 4 hours. The hot solution was filtered, and the filtrate was diluted with 400 ml. of water. Acidification of the solution with concentrated hydrochloric acid, filtration and drying of the solid afforded 15 g. (51%) of crude DL-*cis*-9,10-methyleneoctadecanoic acid, m.p. 31–35°. Two crys-

tallizations from petroleum ether at –30° raised the melting point to 34–37°. Liquid–solid countercurrent distribution of the urea complex of the acid⁴² did not reveal the presence of any impurities and raised the melting point to 36–38°. The infrared spectrum showed characteristic cyclopropane absorption at 3.25 and 9.90 μ and was identical with the published spectrum of dihydrostercularic acid.^{43b} The amide was prepared and melted at 87–88° (lit.,¹⁸ m.p. 86.4–87.6°).

Acknowledgment.—The authors acknowledge with pleasure the many helpful discussions with Dr. B. C. McKusick.

(42) W. N. Sumerwell, *THIS JOURNAL*, **79**, 3411 (1957).

(43) (a) Dihydrostercularic acid has been reported to have m.p. 38.8–39.8° by J. R. Nunn, *J. Chem. Soc.*, 313 (1952), and (b) m.p. 39.7–40.5° by K. Hofmann, O. Jucker, W. R. Miller, A. C. Young, Jr., and F. Taussig, *THIS JOURNAL*, **76**, 1799 (1954). (c) Synthetic DL-*cis*-9,10-methyleneoctadecanoic acid has been reported to have m.p. 38.6–39.6°.¹⁸

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Conjugation in Cyclopropanes. Attempted Acylation, Alkylation, Cyanoethylation and Deuterium Exchange¹

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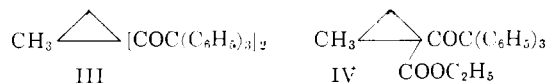
Attempts to effect acylation, alkylation and cyanoethylation of diethyl 2-methylcyclopropane-1,1-dicarboxylate (I) and 1-benzoyl-1,2,2-trimethylcyclopropane (II) failed. Attempted deuterium exchange with I, II, V and IX using sodium amide gave very low exchanges. These results are interpreted as indicating that transmission of electronic effects by the cyclopropane ring to methyl groups beta to electron-withdrawing groups is small in the transition state for carbanion formation.

This paper describes attempts to chemically detect the transmission of conjugative effects to methyl groups by the cyclopropane ring.²

Our first effort to determine if there is transmission of electronic effects to contiguous methyl groups was the prosaic attempt to effect reactions typical of "active methyl" groups. Diethyl 2-methylcyclopropane-1,1-dicarboxylate (I) and 1-benzoyl-1,2,2-trimethylcyclopropane (II), neither of which has α -hydrogen atoms, were synthesized for this purpose. The reactions attempted were acylation with diethyl oxalate and benzoyl chloride, alkylation with alkyl halides and cyanoethylation. Sodium amide, sodium hydride, triphenylmethylsodium and potassium *t*-butoxide were employed as bases. The results of a number of these attempts are summarized in Table I. From 45 to 80% of the starting cyclopropanes were recovered,³ none of the expected reaction products could be isolated and, with the exception discussed later, the cyclopropanes appeared to be essentially inert to the bases. For example, ketone II required 24 hours of refluxing with triphenylmethylsodium to change the color from blood-red to orange, only traces of ammonia were evolved on treatment with sodium

amide and none of the anticipated reaction products could be isolated. These negative experiments are not very satisfying because small amounts of product may have escaped isolation.⁴ However, the fact that glyoxylations at the γ -carbon of α,β -unsaturated esters, ketones and nitriles under comparable or less drastic conditions readily give products in 80–90% yields⁵ and our own experience with conventional cases of these reactions lead us to believe that the formation of the expected products in appreciable quantity would have been detected.

The residue obtained from the attempted alkylation of I with methyl chloromethyl ether and triphenylmethylsodium (expt. 9) was refluxed with sodium hydroxide. Triphenylacetic acid (15% based on triphenylmethylsodium) was isolated. A possible source of the acid is cleavage by hydroxide ion of compounds III and/or IV formed by reac-



tion of triphenylmethylsodium with the carboethoxy groups of I. Support for this assumption is found

(1) Taken from the Ph.D. Theses of Popkin Shenian (1955) and Arthur A. Santilli (1958). This work was supported in part by the Office of Ordnance Research, U. S. Army, and a grant from the University of Massachusetts Teachers' Research Fund.

(2) For an excellent summary of the status of the problem of transmission of conjugation by the cyclopropane ring and leading references see E. N. Trachtenberg and G. Odian, *THIS JOURNAL*, **80**, 4018 (1958).

(3) Triphenylmethylsodium was used in all reactions in which the cyclopropane recovery was less than 65% and large residues remained. The low recoveries were due at least in part to difficulty in separating triphenylmethane from the reaction mixtures.

(4) A further criticism of this approach made by a referee is that "even if products were isolated in all cases showing that reactions other than those of the active methyl type had occurred, one is then in the unfortunate position of not knowing whether the active methyl type reaction has been shielded from view by the incurrence of some faster process."

(5) A. Lapworth, *J. Chem. Soc.*, **79**, 1276 (1901); W. Borsche and R. Manteuffel, *Ber.*, **65B**, 868 (1932); W. Borsche and R. Manteuffel, *Ann.*, **512**, 97 (1934); R. C. Fuson, R. E. Christ and G. M. Whitman, *THIS JOURNAL*, **58**, 2450 (1936); R. E. Christ and R. C. Fuson, *ibid.*, **59**, 893 (1937).

TABLE I
 ATTEMPTED ACYLIATIONS, ALKYLATIONS AND CYANOETHYLATION

Expt.	Cyclopropane ^a	Mole	Base	Mole	Time, ^b hr.	Reactant	Mole	Time, ^c hr.	Cyclopropane recovered, %
1	I	0.2	(C ₆ H ₅) ₃ CNa	0.2		Self-cond.		144	40
2	I	.25	NaNH ₂	.5	3	(COOC ₂ H ₅) ₂	0.25	3	80
3	I	.17	NaH	.17	20	(COOC ₂ H ₅) ₂	.17	14	65
4	I	.2	(C ₆ H ₅) ₃ CNa	.2	3	(COOC ₂ H ₅) ₂	.2	15	45
5	I	.25	(CH ₃) ₃ COK	.5	3.5	(COOC ₂ H ₅) ₂	.3	5	76
6 ^d	I	.22	NaNH ₂	.22	92	CH ₃ I	.3	20	68
7 ^d	I	.167	NaNH ₂	.167	5	C ₂ H ₅ I	.21	5	75
8	I	.125	Triton B	(5 g.)		CH ₂ =CHCN	.155	6 ^e	95
9 ^f	I	.1	(C ₆ H ₅) ₃ CNa	0.1	0.25	CH ₃ OCH ₂ Cl	.1	2	45
10	II	.048	NaNH ₂	.051	20 ^g	C ₆ H ₅ COCl	.051	24	65
11	II	.10	(C ₆ H ₅) ₃ CNa	.1	25.5 ^h	C ₆ H ₅ CH ₂ Cl	.1	12	64

^a I = diethyl 2-methylcyclopropane-1,1-dicarboxylate; II = 1-benzoyl-1,2,2-trimethylcyclopropane. ^b Reflux period before addition of reactant. ^c Reflux period after addition of reactant. ^d Only traces of ammonia liberated during reflux period. ^e Last 4 hours at 60°. ^f Five grams of the reaction mixture residue was refluxed for 2 hours with 1 g. of sodium hydroxide and 18 g. of water and then extracted with ether. After acidification (concd. hydrochloric acid) of the aqueous phase there was obtained 0.6 g. of triphenylacetic acid, m.p. 255–265° (cap.) after recrystallization. ^g Little ammonia liberated during 20-hour reflux. ^h No immediate loss of triphenylmethylsodium color; reaction mixture orange after 24 hours.

 TABLE II
 DEUTERIUM EXCHANGE

Cyclopropane	Mole	NaNH ₂ , mole	D ₂ O, mole	B.p. °C.	Mm.	n _D ²⁰	Atoms D/molecule (× 10 ⁻²)
1,2,2-(CH ₃) ₃ C ₃ H ₂ COOC ₂ H ₅ (V)	0.024	0.026	0.035	57	11	1.4269	0.667 ± 0.058
1-CH ₃ C ₃ H ₄ COOC ₂ H ₅ (VI)	.03	.04	.05	68–68.5	63.5	1.4184	.273 ± .054
2-CH ₃ C ₃ H ₅ (COOC ₂ H ₅) ₂ (I)	.022	.026	.035	80	2	1.4330	.594 ± .029
C ₃ H ₄ (COOC ₂ H ₅) ₂ (VII)	.027	.03	.04	75	2	1.4322	.279 ± .026
1,2,2-(CH ₃) ₃ C ₃ H ₂ COC ₆ H ₅ (II)	.031	.04	.05	95–96.5	2	1.5328	1.46 ± .04
1-CH ₃ C ₃ H ₄ COC ₆ H ₅ (VIII)	.023	.026	.035	89.5	1.5	1.5306	0.174 ± .022
1,2,2-(CH ₃) ₃ C ₃ H ₂ CN (IX)	.03	.04	.05	71.5	36.5	1.4285	.310 ± .020

in the observation of Piehl and Brown⁶ that ethyl cyclopropanecarboxylate reacts with triphenylmethylsodium to give cyclopropyl triphenylmethyl ketone.⁷

In view of the inconclusiveness of the results from this first approach, deuterium exchange was turned to as a more sensitive method for detecting the activation of methyl groups. The strong base lithium diisopropylamide appeared attractive for deuterium exchange studies because it exclusively attacks the α -hydrogen of ethyl isobutyrate rather than the carbonyl group.⁸ However, gentle refluxing occurred when one equivalent of ester V was added to an ether solution of lithium diisopropylamide. From this reaction mixture none of the original ester was recovered, but a small amount of high boiling nitrogen-containing liquid having a carbonyl stretching frequency at 1637 cm.⁻¹, indicative of an amide, was obtained.⁹ Since the use of triphenylmethylsodium was excluded by its reaction with certain esters, sodium amide remained as

(6) F. J. Piehl and W. G. Brown, *THIS JOURNAL*, **75**, 5023 (1953).

(7) Previously it had been reported [A. H. Corwin and R. C. Ellingson, *ibid.*, **64**, 2098 (1942)] that triphenylmethylsodium does not react with the carbethoxy groups of certain dipyrlylmethanes. In the present study it was found that ethyl 1,2,2-trimethylcyclopropane-1-carboxylate (V) did not discharge the color of the base and the ester could be recovered unchanged, whereas ethyl benzoate and diethyl cyclobutane-1,1-dicarboxylate readily discharged the color. Although steric factors may be responsible at least in part for these behavior differences, it appears that a general conclusion concerning the reaction of triphenylmethylsodium with esters cannot be drawn at this time.

(8) M. Hammell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

(9) The compound was not characterized but may be impure 1,2,2-trimethylcyclopropane-1-N,N-diisopropylcarboxamide.

the base of choice for exchange reactions.¹⁰ With the exception of 1-cyano-1,2,2-trimethylcyclopropane (IX), control exchanges were carried out on the corresponding cyclopropanes without β -methyl groups. The exchanges (Table II) vary from 0.17 to 1.46% of one hydrogen atom per molecule.

Exchanges observed by other workers for compounds containing active hydrogens indicate that appreciable activation of the β -methyl groups in the cyclopropanes would have been manifested by higher exchange values. For example, under conditions similar to those employed in the present work methyl norcamphane-1-carboxylate without α -hydrogens exchanged 2.8% of one hydrogen whereas methyl bicyclo[2,2,2]octane-2-carboxylate with one α -hydrogen exchanged 89% of one hydrogen.¹¹ Exchange of the γ -hydrogens of α,β -unsaturated systems has been observed also. Thus exchange occurs readily at the β -methyl groups of diisobutenyl and isobutenyl vinyl ketones¹² and significant exchanges have been reported for the ethyl esters of crotonic, sorbic and β,β -dimethylacrylic acids.¹³

We conclude that all exchanges observed with the cyclopropanes in the present study are of the order

(10) Some amide formation does occur with ethyl 1-methylcyclopropane-1-carboxylate (VI), but this can be minimized by carrying out the exchange at room temperature.

(11) W. P. Whelan, Jr., Ph.D. Thesis, Columbia University, 1952. The author states that exchange with the first ester may be lower because of possible contamination with deuteriotriphenylmethane.

(12) D. N. Kursanov and A. N. Parnes, *Doklady Akad. Nauk S. S. S. R.*, **91**, 1125 (1953); *C. A.*, **48**, 10549 (1954).

(13) W. G. Brown and K. Eberly, *THIS JOURNAL*, **62**, 113 (1940).

of magnitude expected from random exchange with a molecule without active hydrogen atoms. These small exchanges provide strong evidence that transmission of conjugative effects in the transition state for carbanion formation are small indeed in comparison with those commonly observed for analogous α,β -unsaturated esters, nitriles and ketones. Furthermore, they explain the failure to isolate products from the reactions attempted earlier since carbanion formation is an essential step in these reactions.

Experimental

The preparation of the cyclopropanes has been described.¹⁴ Deuterium oxide (>99.5%) was purchased from the Stuart Oxygen Co., San Francisco, Calif.

General Procedure for Attempted Acylation and Alkylation Reactions.—The reaction flask was fitted with a Hershberg stirrer, a reflux condenser protected with a drying tube and a dropping funnel. Sodium amide and sodium hydride were weighed and transferred and triphenylmethylsodium¹⁵ was siphoned into the reaction flask under an atmosphere of nitrogen. Anhydrous ether was used as the solvent in all experiments except no. 5 (*t*-butyl alcohol). A solution of the cyclopropane was added dropwise to the stirred suspension of the base, and the reaction mixture was refluxed with stirring when the addition had been completed. After the specified reaction time a solution of the alkyl halide, or ester, was added dropwise and refluxing continued for the indicated period. The reaction mixture was cooled in an ice-bath and the excess base was decomposed by the cautious addition of ice. The mixture was acidified, the layers sepa-

(14) G. W. Cannon, A. A. Santilli and P. Shenian, *THIS JOURNAL*, **81**, 1660 (1959).

(15) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

rated, and the aqueous phase extracted with solvent. The combined organic phase was washed with sodium bicarbonate and water and dried. After removal of solvent the reaction mixture was fractionated. The results of these attempted reactions are summarized in Table I.

Cyanoethylation reactions were carried out according to the directions of Bruson¹⁶ for the cyanoethylation of diethyl malonate.

Deuterium Exchange.—The procedure described is typical of the exchange reactions. To a stirred suspension of 1.56 g. (0.04 mole) of sodium amide in 150 ml. of dry ether was added 3.3 g. (0.031 mole) of 1-cyano-1,2,2-trimethylcyclopropane (IX). After refluxing for 24 hours, the reaction mixture was cooled in ice and 1.02 g. (0.05 mole) of deuterium oxide was added. The ice-bath was removed and stirring was continued for 3 hours. The ether solution was then dried by the addition of 1 g. of anhydrous sodium sulfate. After removal of the ether, the residue was fractionated through a Todd column (reflux ratio 100:1) yielding 2.1 g. of nitrile, b.p. 66° (29.5 mm.), n_D^{25} 1.4285.

Deuterium Analyses.—About 500 mg. of each compound was combusted according to the procedure of Niederl and Niederl¹⁷ using the universal packing. The water produced in the combustion was collected and purified by the procedure described by Doering and Hoffmann.¹⁸ The deuterium analyses were done at Yale University by the falling drop method.¹⁹

(16) H. A. Bruson in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 79.

(17) J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 108.

(18) W. von E. Doering and A. K. Hoffmann, *THIS JOURNAL*, **77**, 521 (1955).

(19) A. S. Keston, D. R. Henberg and R. Schonheimer, *J. Biol. Chem.*, **122**, 227 (1937). The authors are grateful to Prof. Doering for the use of their falling drop apparatus and to Mr. Marvin Lehr for his invaluable assistance in the actual deuterium determinations.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. VI. The Pyrolysis of 1,3-Dihydroisothianaphthene-2,2-dioxide: A New Synthesis of Benzocyclobutene¹

BY M. P. CAVA AND A. A. DEANA

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The pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide (V) in the molten state at 280–300° gives sulfur dioxide and low yields of a mixture of *o*-xylene, benzocyclobutene (VI) and 1,2,5,6-dibenzocyclooctadiene (VII). In boiling diethyl phthalate solution, the only hydrocarbon formed from V is the octadiene VII. In contrast, decomposition of V in the gas phase over a hot wire at 460–670° gives pure benzocyclobutene in good yield. The primary pyrolysis product of V is *o*-quinodimethane (VIII), as was shown by trapping VIII with *N*-phenylmaleimide to give the *N*-phenylimide of tetralin-*cis*-2,3-dicarboxylic acid (IX).

The synthesis of the benzocyclobutene ring system has been reported by only two routes: the reaction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene with sodium iodide,^{2–4} and the photolysis of α -diazoindanones.^{5,6}

A new synthesis of this system now has been achieved.⁷

(1) Presented before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society in Chicago, Ill., September 8, 1958.

(2) H. Finkelstein, Inaugural Dissertation, Strassbourg, 1910.

(3) M. P. Cava and D. R. Napier, *THIS JOURNAL*, **79**, 1701 (1957).

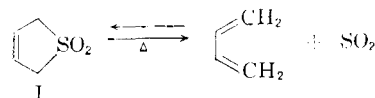
(4) For a closely analogous synthesis from a dibromo-*o*-xylene derivative; see F. R. Jensen and W. E. Coleman, *ibid.*, **80**, 6149 (1958).

(5) M. P. Cava, R. L. Little and D. R. Napier, *ibid.*, **80**, 2257 (1958).

(6) L. Horner, W. Kirmse and K. Muth, *Chem. Ber.*, **91**, 430 (1958).

(7) An additional synthesis of benzocyclobutene, starting with cycloheptatriene, was reported very recently; A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 283 (1958).

It is well known that sulfur dioxide can add to butadiene to give 2,5-dihydrothiophene-1,1-dioxide (I),⁸ a reaction which can be reversed with ease by heat.



The investigation reported here was carried out in order to determine the feasibility of extending the reverse reaction to the cyclic aromatic analog of I, 1,3-dihydroisothianaphthene-2,2-dioxide (V). Only one report of the thermal decomposition of a derivative of V is to be found in the literature: 1,1,3-tri-

(8) E. H. Rodd, ed., "Chemistry of Carbon Compounds," Vol. IV, Part A, Elsevier Publishing Co., New York, N. Y., 1957, p. 221.