853 cm.$^{-1}$ (distinctive finger-print bands for this material), and 780 and 740 cm.$^{-1}$ (probably *cis* olefin). The expected cyclic olefin band at 1615 cm.$^{-1}$ was very weak.

4,7-Bis(2'-cyanoethyl)-4,6-decadienedinitrile (II).—When 8.9 g. (0.027 mole) of 2,2,5,5-thiophenetetrapropionitrile 1-dioxide was heated at 195–205°, 0.1-mm. pressure, for 4 hr., gas evolved leaving a crystalline solid (90% yield). After recrystallization from acetonitrile it melted at 150–151°.

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04; mol. wt., 266. Found: C, 72.21; H, 6.47; N, 20.72; mol. wt., 253 (thermistor micromethod[7] with acetonitrile as the solvent).

Its infrared spectrum showed bands at 2250 cm.$^{-1}$ (nitrile), 1605 cm.$^{-1}$ (conjugated diene), and 1425 cm.$^{-1}$ (—CH_2CN). There were no sulfone bands at 1295 and 1130 cm.$^{-1}$. The ultraviolet spectrum (in acetonitrile solution) showed bands at 243 mμ (sh, ϵ 27,500), 247 mμ (ϵ 28,900), and 255 mμ (sh, ϵ 20,200). This pattern is typical of a poly-substituted linear conjugated diene.

Acknowledgment. The author wishes to thank Mr. N. B. Colthup, Dr. R. C. Hirt, and Mr. R. G. Schmitt for their interpretation of the infrared and ultraviolet spectra, and Mr. R. J. Francel for his cooperation in the analyses.

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[7] A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961).

The Chloromethylation of 5-Nitrosalicylaldehyde

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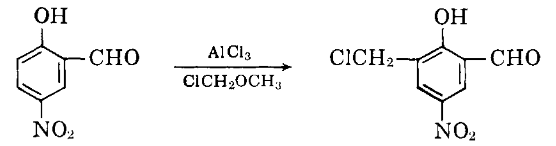
Recently we have had occasion to prepare 3-chloromethyl-5-nitrosalicylaldehyde. We decided to try the direct chloromethylation of 5-nitrosalicylaldehyde, although the aromatic ring is somewhat inactive. After several unsuccessful conventional reactions,[1] a Friedel–Crafts type reaction with aluminum chloride and chloromethyl methyl ether was tried, although aluminum chloride usually is much too active a catalyst for this type of reaction, yielding diphenylmethane compounds. We now have found that chloromethylation of 5-nitrosalicylaldehyde is accomplished in yields of 90% by employing four equivalents of aluminum chloride (one for each oxygen atom) plus a 10% catalytic excess and by carrying out the reaction in pure chloromethyl methyl ether. Several reactions in chloromethyl methyl ether, with zinc chloride or with only one equivalent of aluminum chloride, yielded only starting material. The success of this reaction may be aided by the noticeable solubility of the salicylaldehyde–aluminum chloride complex in chloromethyl methyl ether. The literature does not mention the application of the halo ether as the solvent and it is possible that other highly oxygenated compounds may be successfully chloromethylated by means of this method.



Experimental

Into a 2-l, three-necked, round-bottom flask, fitted with a mechanical stirrer, addition tube, 1 Allihn condenser surmounted by a Friedrichs condenser fitted with a calcium chloride drying tube, were placed 95 g. (0.57 mole) of 5-nitrosalicylaldehyde (m.p. 126–127°, Eastman product) and 1 l. of chloromethyl methyl ether (b.p. 58°, Eastman product). To this solution, cooled to 5°, was added with stirring 312 g. of aluminum chloride (2.3 moles) over a 1-hr. period. This slurry was brought to room temperature and then allowed to reflux for 80 hr. until evolution of hydrogen chloride ceased. The viscous solution was cooled to room temperature and then poured with stirring into 3 l. of crushed ice. The resulting brown tar was stirred with ice–water for ~30 min.

$$ClCH_2OCH_3 + H_2O \longrightarrow H_2O + HCl + CH_3OH$$

The brown solid was filtered and the filtrate extracted with ether. The ether extract was dried with sodium sulfate and the ether was removed by evaporation. The brown solid was added to that previously obtained and the product was recrystallized from carbon tetrachloride using charcoal. In this manner 108 g. (89%) of a tan solid (m.p. 89–90°) was obtained. A small portion was recrystallized from hexane (needles), m.p. 90.5–91.5°.

Anal. Calcd. for $C_8H_6ClNO_4$: C, 44.6; H, 2.8; N, 6.5; Cl, 16.5. Found: C, 44.4; H, 2.8; N, 6.6; Cl, 16.7.

An n.m.r. spectrum of the product is in accord with the assigned structure. The compound, run in deuteriochloroform, showed the following bands: one hydroxyl hydrogen at 12.1 p.p.m., one aldehyde hydrogen at 10.1 p.p.m., two aromatic hydrogens at 8.60 p.p.m., and two methylene hydrogens at 4.70 p.p.m. The only band split was that of the aromatic hydrogens, revealing an AB system with a coupling constant of 3 c.p.s., characteristic of aromatic protons in the *meta* position.[2]

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[1] R. C. Fuson and C. H. McKeever, "Organic Reactions," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 66–71.

[2] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

The Preparation of 1-Aryl-1,2-cyclopropanedicarboximides. An Application of Dimethylsulfoxonium Methylide

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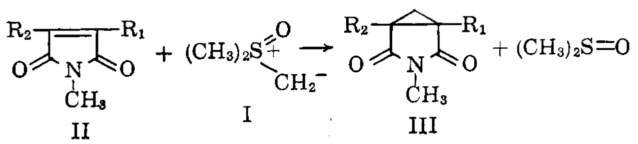
The interest, in these laboratories, in 1-aryl-1,2-cyclopropanedicarboximides as pharmacologically interesting compounds prompted an investigation of new methods for the preparation of some members of this class of substances.

Recently Corey and Chaykovsky[1] have reported on a new synthesis of cyclopropanes based on Michael addition of dimethylsulfoxonium methylide (I) to appropriate α,β-unsaturated ketones. The purpose of this paper is to describe an application of this reaction in which some N-methyl-2-arylmaleimides (II) were the substrates for the action of the ylide. In



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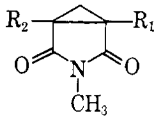
[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

TABLE I

N-METHYL-1-ARYL-1,2-CYCLOPROPANEDICARBOXIMIDES (III)



	R_1	R_2	M.p., °C.	Yield, %	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIIa	C_6H_6	H	55–57[a]	21[b]	$C_{12}H_{11}NO_2$	71.62	5.51	6.96	71.83	5.79	6.62
IIIb	C_6H_6	C_2H_5	113–114[a]	81	$C_{14}H_{15}NO_2$	73.34	6.59	6.11	73.12	6.93	6.03
IIIc	3,4,5-Trimethoxyphenyl	H	136–138[a]	21[c]	$C_{15}H_{17}NO_5$	61.85	5.88	4.81	61.94	6.12	5.01

[a] From alcohol. [b] The low yield was partly the result of difficulty of separation from by-products. In this case, an evaporative distillation and three recrystallizations from alcohol were necessary to bring the compound to analytical purity. [c] Same as in footnote *b*. To achieve purification, repeated fractional crystallizations from alcohol were necessary. The same result could be obtained more conveniently by chromatography of the crude product, using Florisil as adsorbent and benzene and chloroform as the developing and eluting solvents.

the three cases tried the expected 1-aryl-1,2-cyclopropanedicarboximides (III) were formed.

All the reactions were carried out in boiling tetrahydrofuran after first generating I in the same solvent by treating trimethylsulfoxonium chloride with sodium hydride. The results are summarized in Table I.

The evidence for the structure of the cyclopropane products was provided by infrared and ultraviolet spectra, elementary analyses, and unsaturation tests. The infrared spectra of all three compounds, taken in chloroform solution, displayed the typical five-membered cyclic imide doublet at 5.60 and 5.83 μ.[2] A band at 9.74 μ, ascribable to the cyclopropane ring,[3] was present in the spectrum of IIIa and IIIc but absent in that of IIIb. The ultraviolet spectra, taken in methanolic solutions, showed no bands above 220 mμ except for phenyl absorption (IIIa, λ_{max} 250 mμ, ϵ 500; IIIb, λ_{max} 250 mμ, ϵ 690; IIIc, λ_{max} 265 mμ, ϵ 870). The absence of double bonds in all three compounds was also demonstrated by negative tests with bromine in carbon tetrachloride, and potassium permanganate in acetone.

Experimental[4]

Trimethylsulfoxonium Chloride.—This compound was prepared by the method of Kuhn and Trischmann,[5] m.p. 215–216° dec. In spite of extensive purification procedures, and acceptable elementary analyses, the infrared spectrum of this compound, taken on a mineral oil mull, showed bands at 2.78 and 6.22 μ. The intensity of these bands seemed to vary from sample to sample, and in at least one case, they were absent altogether. However, since the reagent gave successful results when used in the reaction, these bands were deemed to be extraneous.

General Procedure for the Preparation of N-Methyl-1-aryl-1,2-cyclopropanedicarboximides.—To a stirred suspension, under nitrogen, of 0.29 g. (0.012 mole) of sodium hydride (from 0.53 g. of a 54.7% oil dispersion) in 150 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added in one lot 1.5 g. (0.012 mole) of trimethylsulfoxonium chloride. As the mixture was heated to reflux, a vigorous evolution of hydrogen ensued. Stirring under reflux was maintained for 45–60 min. and then the N-methyl-2-arylmaleimide (0.012 mole) was added rapidly either as a concentrated tetrahydrofuran solution (10 ml.) or, if insoluble, as a solid in one lot. Following this, the reaction was held at reflux for about 2 hr. and cooled. A few milliliters of absolute alcohol were added to ensure complete destruction of any unchanged sodium hydride and the solvent was removed by distillation at reduced pressure. The invariably dark-colored residue was taken up in 100 ml. of methylene chloride. Alkaline materials were washed out of the solution by three washings with water. The solution was dried ($MgSO_4$) and evaporated to an oily material which usually crystallized after triturating with petroleum ether. This material was then either recrystallized from alcohol or treated as described in Table I.

2-Bromo-N-methyl-2-phenylsuccinimide.—A mixture of 37.8 g. (0.20 mole) of N-methyl-2-phenylsuccinimide,[6] 39.2 g. (0.22 mole) of N-bromosuccinimide, 0.4 g. of benzoyl peroxide, and 800 ml. of carbon tetrachloride was stirred and heated under reflux for 24 hr. and then stored for 16 hr. at room temperature. The nearly theoretical amount (20.8 g.) of succinimide, which floated on top of the solution was filtered and the filtrate was concentrated to about one half volume and cooled in ice. The crystalline product which precipitated (m.p. 107–112°, 49.2 g., 93%) was collected by filtration. Recrystallizations from a mixture of benzene and petroleum ether (b.p. 65–90°) and from aqueous acetone gave colorless crystals, m.p. 110.5–112°.

Anal. Calcd. for $C_{11}H_{10}NO_2Br$: C, 49.26; H, 3.76; N, 5.22; Br, 29.81. Found: C, 49.24; H, 3.80; N, 5.24; Br, 30.04.

N-Methyl-2-phenylmaleimide.—A 7.5-g. (0.028 mole) sample of 2-bromo-N-methyl-2-phenylsuccinimide was dissolved in 75 ml. of anhydrous benzene, and 3 g. (0.03 mole) of triethylamine dissolved in 10 ml. of benzene was added. A precipitate of triethylamine hydrobromide formed immediately and a moderate exothermic effect was noted. The mixture was cooled and allowed to remain at room temperature for 1 hr. The triethylamine hydrobromide was removed by filtration and the benzene filtrate was washed with 0.1 *N* hydrochloric acid and with water, and dried ($MgSO_4$). Concentration at reduced pressure to a small volume and cooling in ice caused the precipitation of yellow needles, m.p. 145.5–148°. The yield was 3.7 g. (71%). A recrystallization from acetone gave pale yellow needles, m.p. 147–148° (lit.[7] m.p. 145–147°). The ultraviolet spectrum showed λ_{max} 222 (ϵ 12,500), 266 (ϵ 9300), and 339 mμ (ϵ 3500).

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.37; H, 4.99; N, 7.23.

2-Chloro-3-(3′,4′,5′-trimethoxyphenyl)succinimide.—This compound was prepared by the arylation of maleimide with 3,4,5-trimethoxyphenyldiazonium chloride following a procedure described by Rondestvedt and Vogl.[8] It was obtained as a yellow crystalline product in 27% yield, after recrystallization from acetone, m.p. 207–208° dec.

Anal. Calcd. for $C_{13}H_{14}NO_5Cl$: C, 52.09; H, 4.71; N, 4.67; Cl, 11.83. Found: C, 51.78; H, 4.61; N, 4.70; Cl, 11.68.

2-(3′,4′,5′-Trimethoxyphenyl)maleimide.—A 2-g. (0.0066 mole) sample of 2-chloro-3-(3′,4′,5′-trimethoxyphenyl)succinimide was mixed with 8 ml. of 2,6-lutidine, and the mixture was heated on a steam bath for 30 min. Then 20 ml. of water was added and the crystals were filtered and recrystallized from chloroform to give 1.5 g. (90%) of yellow needles, m.p. 211–213°.

Anal. Calcd. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 58.93; H, 5.44; N, 5.50.

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(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., J. Wiley and Sons, Inc., New York, N. Y., 1958, p. 221.

(3) L. J. Bellamy, *ibid.*, p. 29.

(4) All melting points were determined in an open capillary tube and are uncorrected. The ultraviolet spectra were taken in methanol on a Cary recording spectrophotometer and the infrared spectra were determined in chloroform with a Perkin-Elmer spectrophotometer (Model 137).

(5) R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

(6) Generously supplied by Parke, Davis and Co., Detroit, Mich.

(7) C. A. Miller, U. S. Patent 2,831,867 (1958).

(8) C. S. Rondestvedt and O. Vogl, *J. Am. Chem. Soc.*, **77**, 2313 (1955).

N-Methyl-2-(3',4',5'-trimethoxyphenyl)maleimide.—To a well stirred suspension of 2.8 g. (0.01 mole) of 2-(3',4',5'-trimethoxyphenyl)maleimide in 75 ml. of freshly distilled tetrahydrofuran (from lithium aluminum hydride), was added 0.24 g. (0.01 mole) of sodium hydride (from 0.45 g. of a 54.7% oil dispersion). There was an immediate evolution of hydrogen which continued briskly as the mixture was brought to reflux. A solution of 7 g. (0.05 mole) of methyl iodide in 10 ml. of tetrahydrofuran was then added to the yellow, boiling, mixture over a 45-min. period, and heating was continued for another 1.75 hr. At the end of this time, the reaction mixture was a dark green color and was neutral to indicator paper. The solvent was distilled at reduced pressure and the residue was dissolved in 75 ml. of chloroform. The chloroform solution was washed twice with water, dried ($MgSO_4$), and evaporated to give 3.1 g. of a deep orange solid. Crystallization from a large volume of hot absolute alcohol in which the material was sparingly soluble (or, from a mixture of ethyl acetate and petroleum ether (b.p. 65–90°)) gave 2 g. (71%) of orange, matted needles, m.p. 155–156°. The ultraviolet spectrum showed λ_{max} 235 (ϵ 13,600), 297 (ϵ 700), and 373 mμ (ϵ 3900).

Anal. Calcd. for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.74; H, 5.71; N, 4.86.

N,5-Dimethyl-3-phenyl-1-pyrazoline-3,4-dicarboximide.—To an ice-cold solution of 8.9 g. (0.048 mole) of N-methyl-2-phenylmaleimide in 150 ml. of methylene chloride was added in one lot a cold, dried (over potassium hydroxide pellets) solution of 0.054 mole of diazoethane in ether.[9] The discharge of the orange-red color was immediate and the final solution retained only a pale yellow color. Evaporation of the solvent and the slight excess of diazoethane gave 11.6 g. (100%) of the crystalline pyrazoline, m.p. 78–85° dec. A sample was purified further by recrystallization from a mixture of methylene chloride and petroleum ether (b.p. 30–60°), giving colorless needles, m.p. 106–107° dec.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.39; N, 17.28. Found: C, 64.74; H, 5.49; N, 17.43.

N-Methyl-2-ethyl-3-phenylmaleimide.—A 5.1-g. (0.02 mole) sample of the crude pyrazoline (m.p. 78–85° dec.) obtained as described was dissolved in 50 ml. of alcohol and heated on a steam bath for 30 min. There ensued an immediate and rapid evolution of nitrogen. The alcohol was removed by distillation *in vacuo* to give 4.4 g. (100%) of a viscous, colorless oil. This material was subjected to partition chromatography in which the system, *n*-heptane–Methyl Cellosolve, was used. This procedure led to the separation of a major and a minor component. The desired N-methyl-2-ethyl-3-phenylmaleimide was the minor and faster moving component. It was obtained by the evaporation of the solvent in the first peak to give 200 mg. (5%) of solid. Two recrystallizations from aqueous alcohol gave large rhombs, m.p. 69–70°. This compound gave positive tests for unsaturation with bromine in carbon tetrachloride and with potassium permanganate in acetone. The ultraviolet spectrum showed λ_{max} 225 (ϵ 13,500), 260 (ϵ 6000), and 331 mμ (ϵ 1500).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.69; H, 5.74; N, 6.37.

The second and slower moving component, obtained as a colorless, viscous oil, was the main product. This was the expected, N,3-dimethyl-1-phenyl-1,2-cyclopropanedicarboximide. The yield was 4.0 g. (93%).[10] This substance could not be crystallized from solvents, even after an evaporative distillation. It did, however, solidify in part after many days at room temperature. The ultraviolet spectrum showed λ_{max} 255 (ϵ 860) as the only band above 220 mμ. The infrared spectrum showed the characteristic succinimide doublet at 5.62 and 5.82 μ.[2]

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.57; H, 6.42; N, 6.25.

Acknowledgment.—The author wishes to thank Mr. L. Brancone and staff for the microanalyses, Mr. C. Pidacks and staff for the separation work by partition chromatography, and Drs. V. J. Bauer and S. R. Safir for helpful suggestions.

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[9] This was prepared from 11.7 g. (0.10 mole) of moist nitrosoethylurea by a procedure analogous to that used for diazomethane (F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

[10] The details of this and other associated work will appear in a future publication.

A Convenient Synthesis of 1,2,5,6-Dibenzocyclooctatetraene[1]

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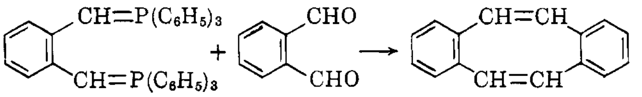
Received January 21, 1963

The Wittig reaction has been applied in several instances for the preparation of cyclic olefins containing five to sixteen carbon atoms and offers a number of advantages over conventional synthetic procedures particularly in the case of larger rings[3]; however, in each of the reported examples, the products have either possessed the *trans* stereochemistry favored by Wittig processes[4] or have been flexible ring systems. In order to determine the limits of applicability of this cyclization procedure, it was of interest to examine a case in which the product was a rigid ring system possessing unfavorable stereochemistry. The model compound chosen for this study was the well characterized 1,2,5,6-dibenzocyclooctatetraene (I),[5-8] for which molecular models indicate a highly rigid *cis* structure,[3a] existing in a tub conformation and incapable of equilibration to a *trans* isomer. The projected synthetic scheme is a simple modification of well established methods,[3a,d] and involves the reaction of the bisylide (II) with *o*-phthaldehyde (III) to form the product (I). The bisylide (II) is readily prepared from *o*-xylylenebis-(triphenylphosphonium bromide) (IV) by the action of base.[3d]



II III I

The reaction of III and IV was first attempted under standard Wittig conditions, *i.e.*, in absolute ethanol employing sodium ethoxide as the base for the generation of the ylide (II).[3d] However, in no instance could I be isolated from reactions carried out under these conditions and the presence of only trace amounts was indicated spectrally; only triphenylphospine oxide, III, and polymeric materials were isolated. Since the Wittig reaction under these conditions leads normally to *trans* olefins,[3d,4] it is probably that the reaction of II and III produces initially *trans*-V, which predominantly undergoes intermolecular reaction to form polymer rather than intramolecular ring closure

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[1] Supported in part by a grant (G-11280) from the National Science Foundation.

[2] National Science Foundation Undergraduate Research Participant, Summer, 1962.

[3] (a) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958); (b) K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); (c) T. I. Bieber and E. H. Eisman, *J. Org. Chem.*, **27**, 678 (1962); (d) C. E. Griffin, K. R. Martin, and B. E. Douglas, *ibid.*, **27**, 1627 (1962); (e) C. E. Griffin and G. Witschard, *ibid.*, **27**, 3334 (1962).

[4] U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959).

[5] L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

[6] A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1668 (1951).

[7] (a) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Ann.*, **572**, 1 (1951); (b) G. Wittig, G. Koenig, and K. Clauss, *ibid.*, **593**, 127 (1955).

[8] M. Avram, D. Dinu, G. Matescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).