350 mg (94%) of crude product. Trituration with ether gave crystals of **8b** which were recrystallized consecutively from acetone–ether, methanol–ether, and petroleum ether (bp 60–80°)–acetone to yield colorless crystals: mp 115–117° (lit.[17] 122°); ir 1680 (w, C=O), 1655 (amide C=O) cm^{-1}; nmr τ 1.97–3.0 (m, 4, aromatic), 5.97, 7.33, and 7.7–8.42 (m, 6, aliphatic), 8.08 (s, 3, $COCH_3$). This sample was characterized by identical ir, uv, and nmr spectra, melting point, and mixture melting point with those of authentic material prepared from the corresponding 1-*p*-toluenesulfonyl derivative **12** according to the method of Proctor.[17]

Registry No.—**2**, 19501-93-0; **3a**, 27150-46-5; **3b**, 27150-47-6; **5a**, 27150-48-7; **5b**, 27150-49-8; **6a**, 27150-50-1; **6b**, 27150-51-2; **7a**, 27150-52-3; **7b**, 27150-53-4; **8a**, 27150-54-5; **9**, 27150-55-6; **11**, 27150-56-7; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8.

Acknowledgments.—The support of this work by the Department of University Affairs, Province of Ontario, and the National Research Council of Canada is gratefully acknowledged. Thanks are also due to the Chemistry Departments of Guelph and McMaster Universities, in particular to Professor G. L. Lange and Mr. B. Sayer, for making their 60-Mc nmr facilities available to us. We are deeply indebted to Dr. K. N. Shaw and Professor L. W. Reeves for the 100-Mc temperature-variable nmr spectra. Dr. G. F. Grail kindly assisted in naming compound **11**.

Novel Cyclizations and Ring-Opening Reactions of 3-Phenylindene Derivatives

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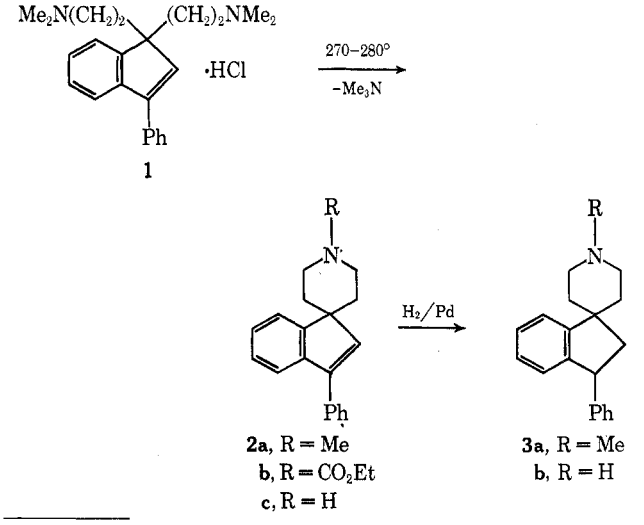
A spiroindenopiperidine **2a** is obtained by pyrolysis of the 1,1-dialkylated 3-phenylindene **1**. However, similar treatment of the 1,3-substituted isomer **4** yields a fused indenopyrrole **5**. Attempted N-demethylation of **5** with ethyl chloroformate causes ring opening to **10**. On refluxing **10** with alcoholic potassium hydroxide, competing intramolecular cyclization to **5** and bimolecular displacement of halogen by ethoxide ion to **12** occurs. Mechanisms of these transformations are discussed.

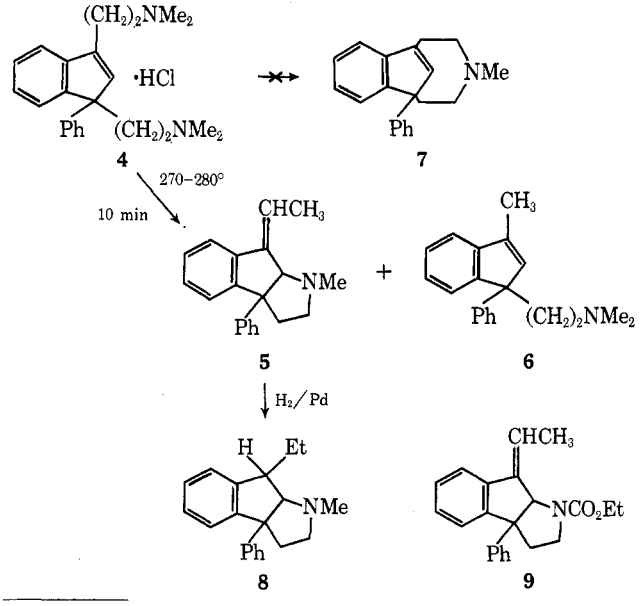
Our interest in alkylamino-3-phenylindene derivatives as CNS agents[1] led us to investigate the synthesis of some phenylindeno- and phenylindano heterocycles. Publications by Dykstra, *et al.*,[1] and by Ganellin, Loynes, and Ansell,[2] established the structure of the products of alkylation of 3-phenylindene with sodium amide and 2-dimethylaminoethyl chloride. They identified three monoalkylated materials as well as the 1,1- and 1,3-dialkylated materials. The present paper discusses some interesting transformations of these dialkylated compounds **1** and **4**.

The dialkylated indenes were obtained by a modification of the previously used method.[2] On pyrolysis of the diamine **1** monohydrochloride, according to the method of Blicke, *et al.*,[3] compound **2a** was isolated in high yield along with trimethylamine.

Treatment of the indene derivative **2a** with ethyl chloroformate[4] yielded the carbamate **2b**, which hydrolyzed to the secondary amine **2c** with ethanolic potassium hydroxide. The spiroindenes **2a** and **2c** were converted to the corresponding indans by hydrogenation over a palladium-on-carbon catalyst.

Pyrolysis of the 1,3-substituted compound **4**, however, did not give the bridged indene **7** but yielded a mixture of products from which **5** (42%) and **6** (9.5%) were separated by column chromatography.





(1) S. J. Dykstra, J. M. Berdahl, K. N. Campbell, C. M. Combs, and D. G. Lankin, *J. Med. Chem.*, **10**, 418 (1967).

(2) G. Ganellin, J. Loynes, and M. Ansell, *Chem. Ind. (London)*, 1256 (1965).

(3) F. F. Blicke, J. A. Faust, J. Krapcho, and E. Tsao, *J. Amer. Chem. Soc.*, **74**, 1844 (1952).

(4) J. D. Hobson and J. G. McCluskey, *J. Chem. Soc. C*, 2015 (1967), and references therein.

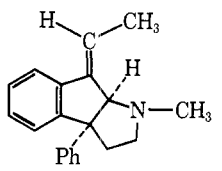
The structure of **5** was established by analysis, and nmr and mass spectra. The nmr spectrum showed **5** to be a 70:30 mixture of isomers (Table I) from which a pure sample of the major isomer was separated by repeated crystallizations of its picrate salt.

TABLE I
NMR SPECTRUM OF 5 IN CCl_4

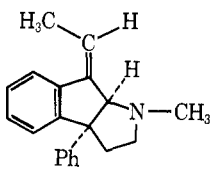
Position, δ, ppm				Multiplicity and coupling constant
Major isomer	Minor isomer	Type or proton	No. of protons	(J in Hz)
7.0–7.9	7.0–7.9	Aromatic	9	m
6.15	5.65	=CH	1	q,[a] 7 Hz
3.73	3.17	>CH	1	s[a]
2.45–2.95	2.45–2.95	$-CH_2CH_2-$	4	m
2.37	2.30	$>NCH_3$	3	s
1.90	2.07	$=CCH_3$	3	d, 7 Hz

[a] Fine splitting ($J \sim 1$ Hz) was also observed.

Four enantiomeric pairs of isomers of **5** are possible owing to geometrical isomerism at the olefinic bond and the possibility of cis or trans fusion of the five-membered rings. Rigorous stereochemical assignments could not be made on the basis of the nmr spectrum. However, since the compounds with cis ring fusion are probably much more stable[5] than the trans-fused isomers, the products **5** are likely to be cis fused as in structures **5a** and **5b**.



5a



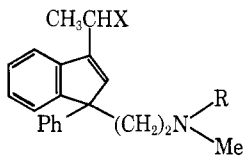
5b

The conversion of a 95:5 mixture of the isomers of **5** to a 65:35 mixture by ultraviolet irradiation provides additional evidence for isomerization at the olefinic bond rather than at the ring junction.

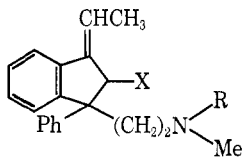
On the basis of the chemical shifts of the olefinic hydrogen atoms, structure **5a** is favored for the major isomer and **5b** for the minor isomer. The chemical shifts in **5a** and **5b** were calculated[6] to be δ 5.86 and 5.57, respectively, which agree well with the values δ 6.15 and 5.65 found for the major and minor isomers (Table I).

The structure of **5** was further confirmed by hydrogenation of its hydrochloride salt over a palladium-on-carbon catalyst to yield **8** HCl. The two doublets due to the *N*-methyl group in the nmr spectrum of **8** HCl showed it to be a 50:50 mixture of two isomers. The same isomer distribution was obtained on hydrogenation of either the pure major isomer of **5** or a mixture of the isomers, in agreement with the expected products from hydrogenation of **5a** and **5b**.

Reaction of **5** with ethyl chloroformate failed to give the expected product **9**. Instead, a product was obtained in quantitative yield which was identified as **10** by its analysis, and nmr and infrared spectra. Structure **10**, rather than **11**, was assigned to the product because the nmr signals for the vinylic and tertiary hydrogen atoms appear as a sharp singlet at δ 6.55 and a quartet at δ 5.15, respectively. Structure **11** would require the quartet, in this case for the vinyl hydrogen atom, to be downfield from the singlet due to the tertiary hydrogen atom.



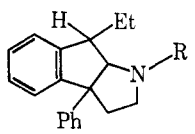
10, R = CO_2Et; X = Cl
12, R = H; X = OEt



11, R = CO_2Et; X = Cl
13, R = H; X = OEt

On refluxing the ethoxycarbonyl compound **10** with ethanolic potassium hydroxide, two products were formed, one of which was identical with **5** (65:35 mixture of isomers) and the other was identified as the ether **12** by its analysis, and nmr and infrared spectra. Structure **13** was ruled out, since the nmr signals due to the vinylic and tertiary hydrogen atoms appeared as a singlet at δ 6.36 and a quartet at δ 4.58, respectively.

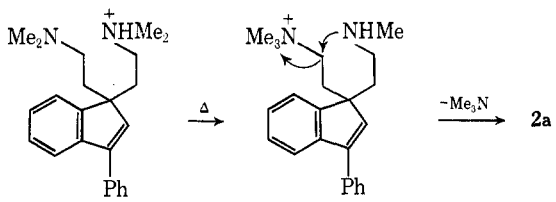
N-Demethylation of compound **8** with ethyl chloroformate occurred normally to yield the ethoxycarbonyl compound **14**, which hydrolyzed with ethanolic potassium hydroxide to the secondary amine **15**.



14, R = CO_2Et
15, R = H

Discussion and Mechanisms

Formation of Compounds 2a and 5.—The formation of the spiro compound **2a** from **1** presumably occurs by an initial intramolecular disproportionation involving migration of a methyl group, followed by nucleophilic displacement of trimethylamine.



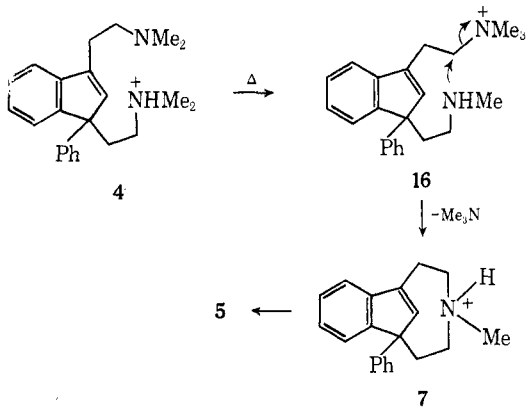
1

A similar mechanism was proposed by Snyder, *et al.*,[7] to account for the formation of dibenzylmethylamine and trimethylamine by heating benzyldimethylamine with an acid catalyst or with a catalytic amount of its methiodide salt.

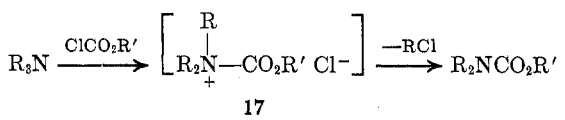
The formation of **5** rather than **7** from **4** may be accounted for by a similar process. In this case, cyclization gives the strained eight-membered ring system **7**, formed *via* **16** by nucleophilic displacement of trimethylamine by the secondary amine function. Due to the close proximity of the *N*-methyl group and the olefinic bond in the eight-membered ring, this species may then

(5) H. Booth, F. E. King, K. G. Mason, J. Parrick, and R. L. St. D. Whitehead, *J. Chem. Soc.*, 1050 (1959).
(6) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).
(7) H. R. Snyder, R. E. Carnahan, and E. R. Lovejoy, *J. Amer. Chem. Soc.*, **76**, 1301 (1954).

undergo transannular rearrangement to yield the observed product **5**. Similar transformations are known to occur during alkaloid degradations.[8]

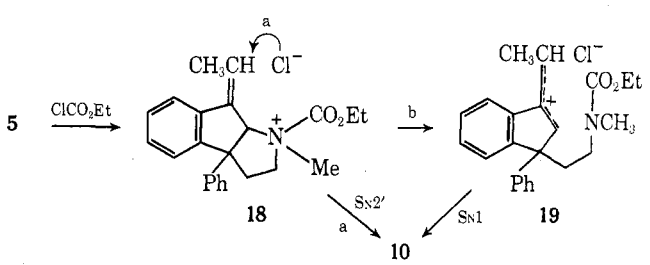


Reaction of 5 with Ethyl Chloroformate.—Chloroformates[4] are well known for their ability to cleave tertiary aliphatic and alicyclic amines to the corresponding dialkyl carbamates *via* the intermediate **17**. The alkyl group that forms the most stable carbonium ion is cleaved.[9]

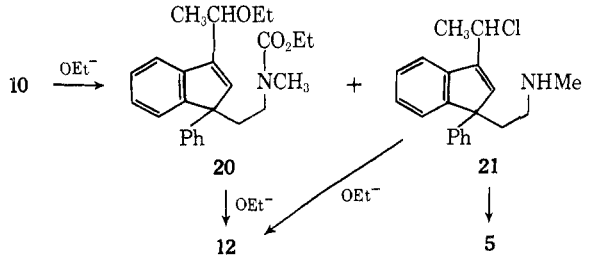


17

In the reaction of **5** with ethyl chloroformate, the chloride ion attacks the allylic carbon atom rather than the *N*-methyl carbon atom. This ring-opening reaction may occur by an S_N2' process (route a), by synchronous displacement of the amino function to give **10**. Alternatively, C–N bond breaking may occur first (S_N1, route b) to afford a resonance-stabilized allylic carbonium ion **19**, which then adds chloride ion.



Hydrolysis of 10.—On refluxing an ethanolic potassium hydroxide solution of **10**, two competing reactions occur. Direct bimolecular displacement of halogen by ethoxide ion yields the intermediate **20**, which hydrolyzes further to **12**. Hydrolysis of the carbamate function before displacement of halogen, however, affords **21**, which then either undergoes intramolecular cyclization to **5** or forms **12** by reaction with ethoxide ion.



(8) K. W. Bentley, "Isoquinoline Alkaloids," 1st ed, Pergamon Press, London, 1965, p 173.

(9) W. B. Wirght, Jr., and H. J. Brabander, *J. Org. Chem.*, **26**, 4057 (1961).

Experimental Section[10]

1,1- and 1,3-Bis(2-dimethylaminoethyl)-3-phenylindene (1 and 4).—A solution of 3-phenylindene[11] (64 g, 0.33 mol) in dry benzene (250 ml) was stirred and refluxed with sodium amide (15.6 g, 0.4 mol) for 1 hr. A solution of 2-dimethylaminoethyl chloride (43 g, 0.4 mol) in dry benzene (100 ml) was added dropwise, and the mixture was stirred and refluxed for 1.5 hr. The cooled mixture, after further treatment with sodium amide (0.4 mol) and 2-dimethylaminoethyl chloride (0.4 mol) as described above, was stirred overnight at 25°. Water was added dropwise to the stirred mixture and the benzene layer was separated, washed with water, and extracted several times with 3 *N* HCl. The combined acid extracts were washed with benzene and made basic with NaOH. The precipitated oil was extracted with ether, washed with water, and dried (anhydrous K_2CO_3) to give a yellow oil (93 g), showing three spots on tlc on silica gel/DMF–ethanol–hexane (3:1:1) at R_f values 0.15, 0.40, and 0.75. The products were separated by the method of Ganellin, Loynes, and Ansell,[2] to afford pure 1-(2-dimethylaminoethyl)-1-phenylindene hydrochloride (21%), **1** dihydrochloride (11%), and **4** dihydrochloride (32%).

Pyrolysis of 1,1-Bis(2-dimethylaminoethyl)-3-phenylindene Hydrochloride (1 HCl).—A solution of **1** (5.0 g, 0.0148 mol) and its dihydrochloride salt (6.0 g, 0.0148 mol) in methanol was evaporated, and the residual oil was heated under reduced pressure (water pump) at 270–280° for 10 min. The evolved gas was collected in a Dry Ice trap and converted to its hydrochloride salt to yield trimethylamine hydrochloride (1.55 g, 54%). The pyrolyzed product was dissolved in chloroform and shaken with 10% NaOH solution. The chloroform layer was separated, washed with water, and dried (anhydrous K_2CO_3). The oil obtained by evaporation of the solvent was identified as ***N*-methyl-3-phenylspiro[indene-1,4′-piperidine] (2a)**: R_f 0.4 on silica gel/MeOH–DMF (9:1); nmr ($CDCl_3$) δ 7.2–7.8 (m, 9 H, aromatic), 6.90 (s, 1 H, =CH), 2.8–3.2 (m, 2 H, ring CH), 2.0–2.8 (m, 3 H, ring CH), 2.43 (s, 3 H, NCH_3), 0.7–1.9 (m, 3 H, ring CH). **2a** was converted to its hydrochloride salt (83%), mp 292–294° dec, which crystallized from isopropyl alcohol–isopropyl ether.

Anal. Calcd for $C_{20}H_{22}ClN$: C, 77.02; H, 7.11; Cl, 11.37. Found: C, 77.15; H, 6.98; Cl, 11.21.

Ethyl 3-Phenylspiro[indene-1,4′-piperidine]-1-carboxylate (2b).—A solution of **2a** (17.6 g, 0.064 mol) in benzene (30 ml) was added dropwise with stirring to a hot solution of ethyl chloroformate (21.7 g, 0.2 mol) in benzene (20 ml). A precipitate formed immediately and the reaction mixture became almost solid. After refluxing the mixture for 6 hr, water and ether were added until all the precipitate dissolved. The layers were separated and the organic phase was extracted with 3 *N* HCl, from which a precipitate of **2a** HCl (1.7 g, 8.5%) separated. The organic layer was dried and evaporated to yield 15.4 g (72%) of crude product, which, on crystallization from absolute ethanol, gave 13.6 g (63.5%) of the ethoxycarbonyl derivative **2b**: mp 116–118°; ir absorption (Nujol) 1695 cm^{-1} [NC(=O)OEt]; nmr ($CDCl_3$) δ 7.2–7.8 (m, 9 H, aromatic), 6.85 (s, 1 H, =CH), 4.2 (q, 2 H, OCH_2, J = 7 Hz), 4.0–4.5 (m, 2 H, ring CH), 1.1–3.5 (m, 6 H, ring CH), 1.30 (t, 3 H, CCH_3, J = 7 Hz).

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; O, 9.60. Found: C, 79.55; H, 6.55; O, 9.90.

3-Phenylspiro[indene-1,4′-piperidine] Hydrochloride Monohydrate (2c HCl).—A solution of the ethoxycarbonyl derivative **2b** (12.5 g, 0.038 mol) in 95% ethanol (80 ml) containing KOH (50 g) was refluxed under nitrogen for 10 hr. The mixture was diluted with water, concentrated under reduced pressure to remove ethanol, and extracted with ether. On shaking the ethereal extract with 2 *N* HCl, a precipitate formed. This solid (10.3 g), mp 220–223°, was filtered off and crystallized from 95% ethanol to yield 9.2 g (76%) of **2c** HCl monohydrate.

(10) Nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as the internal standard. Ir spectra were obtained on a Beckman IR-9 spectrometer. Mass spectra were recorded at 70 eV using a direct inlet system on a Consolidated Electrodynamics CEC Model 21104 instrument. Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected.

(11) K. N. Campbell, U. S. Patent 2,884,456 (1959); *Chem. Abstr.*, **53**, 18931C (1959).

Anal. Calcd for $C_{19}H_{22}ClNO$: C, 72.25; H, 7.02; Cl, 11.23; H_2O, 5.71. Found: C, 72.52; H, 7.30; Cl, 10.98; H_2O, 6.1.

2c (free base): ir absorption (Nujol) 3275 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.1–7.8 (m, 9 H, aromatic), 6.95 (s, 1 H, =CH), 2.7–3.3 (m, 4 H, ring CH), 1.7–2.4 (m, 3 H, NH and ring CH), 1.2–1.6 (m, 2 H, ring CH).

1-Methyl-3-phenylspiro[indan-1,4′-piperidine] (3a).—A solution of the indene **2a** (7.1 g, 0.0257 mol) in absolute ethanol (70 ml) was hydrogenated in a Parr apparatus at 60 psi over a 10% palladium-on-carbon catalyst for 1.5 hr. After removal of the catalyst and solvent, the residue (5.8 g) crystallized from heptane to give 3.7 g (52%) of the indan **3a**: mp 105–108°; nmr ($CDCl_3$) δ 6.8–7.5 (m, 9 H, aromatic), 4.36 (t, 1 H, >CH, J = 9 Hz), 2.33 (s, 3 H, NCH_3), 1.4–3.0 (m, 10 H, ring CH).

Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.33; H, 8.32; N, 4.74.

3-Phenylspiro[indan-1,4′-piperidine] Hydrochloride (3b).—A solution of the indene **2c** (31.3 g, 0.12 mol) in 95% ethanol (100 ml) was hydrogenated in a Parr apparatus at 60 psi over a 10% palladium-on-carbon catalyst for 30 hr. After removal of the catalyst and solvent, the solid residue was dissolved in ether and extracted with 3 N HCl (100 ml). The white precipitate that formed in the aqueous layer was collected and crystallized from 95% ethanol to yield 32 g (81%) of the indan **3b** HCl: mp 238–239.5°.

Anal. Calcd for $C_{19}H_{22}ClN$: C, 76.10; H, 7.40; Cl, 11.83. Found: C, 76.17; H, 7.51; Cl, 11.88.

3b (free base): ir absorption (film) at 3340 cm^{-1} (broad, NH); nmr ($CDCl_3$) δ 6.9–7.5 (m, 9 H, aromatic), 4.45 (t, 1 H, >CH, J = 8 Hz), 1.4–3.3 (m, 11 H, NH and ring CH).

Pyrolysis of 1,3-Bis(2-dimethylaminoethyl)-3-phenylindene Hydrochloride (4 HCl).—A solution of **4** (16.7 g, 0.05 mol) and its dihydrochloride salt (20.3 g, 0.05 mol) in methanol was concentrated to an oil, which was heated under reduced pressure (water pump) at 270–280° for 10 min. Volatile material, that collected in a Dry Ice trap, was identified as trimethylamine by converting it to its hydrochloride salt (3.2 g, 38%). The nonvolatile residue, dissolved in 3 N HCl, was converted to the free base with NaOH and extracted with ether to yield a yellow oil (23 g). Tlc of the oil on silica gel/methanol–DMF (9:1) showed at least four spots at R_f 0.8, 0.6, 0.5, and close to the origin. The oil was chromatographed on silica gel (600 ml).

Elution with ether–petroleum ether (1:3) gave a single product (9.5 g), R_f 0.8, identified by nmr (Table I) as a 70:30 mixture of isomers of **8-ethylidene-1,2,3,3a,8,8a-hexahydro-1-methyl-3a-phenylindeno[2,1-b]pyrrole (5).** The mass spectrum showed a molecular ion at m/e 275, a M + 1^+ peak at 276, and abundant peaks at m/e 246, 232, 219, 218 (base peak), 217, 216, 215, 203, 202, and 44. The free base, in boiling methanol, formed a mucate monohydrate salt, mp 162–164°, which crystallized from methanol–isopropyl ether as a 85:15 mixture of isomers.

Anal. Calcd for $C_{23}H_{28}NO_5$: C, 70.52; H, 6.86; N, 3.78. Found: C, 70.50; H, 6.85; N, 3.53.

Repeated recrystallizations of **5** picrate from ethanol afforded the pure major isomer, mp 198–200°, which was converted to **5** hydrochloride monohydrate, mp 149.5–159°.

Elution with ether–petroleum ether (1:1) gave a yellow oil (3.1 g), R_f 0.6 and 0.5, which was converted to its hydrochloride salt and crystallized several times from acetone to yield 1.8 g (9.5%) of 1-(2-dimethylaminoethyl)-3-methyl-1-phenylindene hydrochloride[12] (6 HCl): R_f 0.5; mp and mmp 197–199°. The other components of the mixture were not identified.

Hydrogenation of 5 HCl. A.—A solution of **5** hydrochloride 3.15 g, 0.02 mol) in ethanol was hydrogenated in a Parr apparatus at 50 psi over a 10% palladium-on-carbon catalyst. After removal of the catalyst and solvent, the residue crystallized from acetone–isopropyl ether to yield 2.6 g (84%) of **8-ethyl-1,2,3,3a,8,8a-hexahydro-1-methyl-3a-phenylindeno[2,1-b]pyrrole hydrochloride (8 HCl)**: mp 154–160°; nmr ($CDCl_3$) δ 3.0 (d, J = 4 Hz) and 2.6 (d, J = 4 Hz) due to N-methyl protons indicates a 50:50 mixture of isomers. **8** (free base): bp 143–146° (0.1 mm); nmr (CCl_4) δ 7.0–7.4 (m, 9 H, aromatic), 2.4–3.2 (m, 6 H, >CH, NCH<, NCH_2), 2.35 (s, 3 H, NCH_3), 0.7–1.7 (m, 5 H, CH_2CH_3). The mass spectrum showed a molecular ion at m/e 277, a M + 1^+ peak at 278, and abundant peaks at m/e 220, 205, 192, 191, 172, 159, 158, 144, 91, 58, 57, 44 (base peak), and 42.

(12) H. Ueberwasser, U. S. Patent 2,798,888 (1957); *Chem. Abstr.*, **52**, 1261 (1958).

Anal. Calcd for $C_{20}H_{23}N$: C, 86.60; H, 8.35; N, 5.05. Found: C, 86.55; H, 8.24; N, 4.99.

B.—The same 50:50 mixture of isomers was obtained by hydrogenation of the pure major isomer of **5** as described above.

Photolysis of 5 HCl.—A solution of **5** hydrochloride (0.2 g, 95:5 isomer mixture) in isopropyl alcohol (25 ml) was irradiated with a short-wave uv lamp UVS-11 for 60 hr. After evaporation of the solvent, the residue was converted to the free base with NaOH. Nmr showed the product to be a 65:35 mixture of the isomers.

Reaction of 5 with Ethyl Chloroformate.—A solution of **5** (5.5 g, 0.02 mol) (85:15 mixture of isomers), in dry benzene (25 ml), was added slowly to a boiling solution of ethyl chloroformate (6.5 g, 0.06 mol) in benzene (15 ml). The solution, after being refluxed for 18 hr, was cooled and washed with 3 N HCl and water. The dried ($MgSO_4$) solution was concentrated to a pale yellow oil (7.5 g), identified as **3-(1-chloroethyl)-1-(2-ethoxycarbonylmethylamino)-1-phenylindene (10)**: R_f 0.4 by tlc on silica gel/chloroform; ir absorption (film) at 1695 cm^{-1} [C(=O)]; nmr (CCl_4) δ 7.0–7.6 (m, 9 H, aromatic), 6.55 (s, 1 H, =CH), 5.15 (q, 1 H, *tert*-CH, J = 7 Hz), 4.1 (q, 2 H, OCH_2, J = 7 Hz), 2.1–3.5 (m, 4 H, CH_2), 2.75 (s, 3 H, NCH_3), 1.95 (d, 3 H, $=CCH_3$, J = 7 Hz), 1.2 (t, 3 H, CCH_3, J = 7 Hz).

Anal. Calcd for $C_{23}H_{26}ClNO_2$: C, 71.97; H, 6.83; Cl, 9.23; N, 3.65. Found: C, 72.19; H, 6.74; Cl, 9.33; N, 3.65.

Hydrolysis of 10.—A solution of the carbamate (5.2 g, 0.0136 mol) and KOH (11.2 g, 0.2 mol) in 95% ethanol (30 ml) was refluxed under nitrogen for 36 hr. The cooled solution was diluted with water and extracted with ether. Basic material was extracted from the ether with 3 N HCl. Product was isolated by basifying the acid solution with 10% NaOH, followed by extraction of the precipitated oil with ether. The ether solution was washed with water, dried (anhydrous K_2CO_3), and concentrated to a yellow oil (3.9 g), which showed spots at R_f 0.8 and 0.35 by tlc on silica gel/methanol–DMF (9:1). The products were separated by column chromatography on silica gel.

Elution with ether–petroleum ether (1:2) gave 1.60 g (43%) of a colorless oil: R_f 0.8; ir and nmr spectra identical with **5**. The nmr spectrum indicated a 65:35 mixture of isomers.

Elution with ether and ether–methanol yielded 2.2 g (50.5%) of **3-(1-ethoxyethyl)-1-(2-methylaminoethyl)-1-phenylindene (12)** as a colorless oil: ir absorption (film) at 3300 (broad, NH), 1100 and 1170 cm^{-1} (COC); nmr ($CDCl_3$) δ 7.1–7.7 (m, 9 H, aromatic), 6.40 (s, 1 H, =CH), 4.60 (q, 1 H, OCH, J = 7 Hz), 3.52 (q, 2 H, OCH_2, J = 7 Hz), 2.3–2.8 (m, 4 H, CH_2CH_2N), 2.30 (s, 3 H, NCH_3), 2.03 (s, 1 H, NH), 1.55 (d, 3 H, $=CCH_3$, J = 7 Hz), 1.22 (t, 3 H, CCH_3, J = 7 Hz). **12** oxalate crystallized readily from isopropyl alcohol, mp 183–184°.

Anal. Calcd for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 70.07; H, 7.02; N, 3.34.

12 hydrochloride, mp 164–166°, crystallized slowly from acetone–isopropyl ether.

N-Demethylation of 8 with Ethyl Chloroformate.—A solution of **8** (2.89 g, 0.01 mol) in dry benzene (20 ml) was added dropwise with stirring to a hot solution of ethyl chloroformate (3.3 g, 0.03 mol) in benzene (5 ml). After refluxing the mixture for 24 hr, solvent and excess ethyl chloroformate were removed under reduced pressure. A solution of the residual oil in ether was washed with 3 N HCl and water. The dried ($MgSO_4$) ether solution was concentrated under vacuum to a pale yellow oil (3.2 g): ir absorption (film) at 1700 cm^{-1} [NC(=O)OEt]; nmr ($CDCl_3$) δ 6.9–7.5 (m, 9 H, aromatic), 4.20 (q, 2 H, OCH_2, J = 7 Hz), 2.0–3.7 (m, 6 H, >CH, NCH< and ring CH), 1.1–1.7 (m, 5 H, $OCCH_3$, CH_2), 0.90 (t, 3 H, CCH_3, J = 7 Hz).

A solution of the oil in 95% ethanol (25 ml), containing KOH (9 g, 0.15 mol), was refluxed under nitrogen for 48 hr. The mixture was cooled, diluted with water, and extracted with ether. Basic material was isolated by extraction of the ether solution with 3 N HCl, basification of the acid extract with 10% NaOH, and extraction of the precipitated oil with ether. Concentration of the dried (anhydrous K_2CO_3) ether solution gave a colorless oil (2.3 g) identified as **8-ethyl-1,2,3,3a,8,8a-hexahydro-3a-phenylindeno[2.1-b]pyrrole (15)**: ir absorption (film) at 3300 cm^{-1} (broad, NH); nmr ($CDCl_3$ δ 7.0–7.6 (m, 9 H, aromatic), 3.73 (broad, 1 H, NCH<), 2.0–3.4 (m, 6 H, ring CH and NH), 1.1–1.8 (m, 2 H, CH_2C), 0.97 (t, 3 H, CCH_3, J = 7 Hz). Compound **15** formed a hydrochloride salt, mp 200–203°, which crystallized from acetone–isopropyl ether.

Anal. Calcd for $C_{19}H_{22}ClN$: C, 76.08; H, 7.30; N, 4.67. Found: C, 76.08; H, 7.33; N, 4.81.

Registry No.—**2a**, 27415-49-2; **2a** HCl, 27415-50-5; **2b**, 27371-44-4; **2c**, 27415-51-6; **2c** HCl, 27415-52-7; **3a**, 27371-45-5; **3b**, 27415-53-8; **3b** HCl, 27415-54-9; **5a**, 27390-80-3; **5a** $^1/_2$-mucate, 27425-33-8; **5a** HCl, 27390-81-4; **5b**, 27390-82-5; **5b** $^1/_2$-mucate, 27494-97-9; *cis,cis*-**8**, 27390-83-6; *cis,cis*-**8** HCl, 27390-84-7; *cis,trans*-**8**, 27390-85-8; *cis,trans*-**8** HCl, 27390-86-9; **10**, 27371-46-6; **12**, 27371-47-7; **12** oxalate, 27371-48-8; **12** HCl, 27371-49-9; **15**, 27415-55-0; **15** HCl, 27415-56-1.

High Pressure Studies. VI. Polar Effects in Decomposition of Substituted *tert*-Butyl Phenylperacetates in Solution[1,2]

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The pressure dependences of the rates of thermal decomposition of the *m*-Cl-, *p*-Cl-, H-, *p*-CH_3-, and *p*-CH_3O-substituted *tert*-butyl phenylperacetates in cumene have been determined. The observed decomposition activation volumes are lower than expected for two-bond homolytic scission reactions and are also pressure dependent. The values of ΔV^*_{obsd} are concluded to be a composite of contributions from bond stretching and solvation of a polar transition state. The data indicate that the polarity of the transition states varies with substituent and also that the pressure dependence of the values of ΔV^*_{obsd} probably resides in the pressure dependence of solvent compressibility.

Activation volumes[3] for homolytic scission reactions in which the primary radical pair cannot return to starting material reflect the pressure dependence of the bond breaking process.[1a,3b,4] Examples of general systems which would be expected to fit this category are azo compounds and peresters, which decompose *via* simultaneous two-bond scission (eq 1 and 2). Activation

$$RN{=}NR \longrightarrow \overline{R\cdot\ N_2\ \cdot R} \qquad (1)$$

$$RCO_2OR' \longrightarrow \overline{R\cdot\ CO_2\ \cdot OR'} \qquad (2)$$

volumes for representative cases (Table I) seem to fall

TABLE I

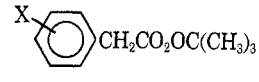
SOME ACTIVATION VOLUMES FOR HOMOLYTIC SCISSION[a]

Compd	T, °C	ΔV^*, cc/mol	Ref
$C_6H_{11}CO_3C(CH_3)_3$	79.6	+3.9	3b, 5a
$(CH_3)_3CON{=}NOC(CH_3)_3$	55.0	+4.3	1a
$C_6H_5C(CH_3)_2N{=}NC(CH_3)_2C_6H_5$	55.0	+4.9	*b*
$NCC(CH_3)_2N{=}NC(CH_3)_2CN$	70.0[c]	+4.0	6

[a] Cumene solvent. [b] R. Neuman and M. Amrich, unpublished results. [c] Toluene solvent.

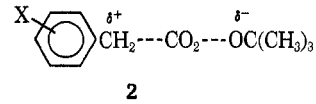
within the range of +4 to +5 cc/mol, and they are relatively constant over a range of several thousand atmospheres.[1a,3b,5,6]

The ring-substituted *tert*-butyl phenylperacetates (**1**) are also thought to decompose by two-bond scission[7,8]



1

and would be expected to show similar behavior in pressure studies. However, we have previously reported that the low pressure activation volume for *tert*-butyl phenylperacetate (**1**, X = H) while positive is significantly lower (+0.5 cc/mol) than those for the compounds in Table I and is pressure dependent.[3b] We have suggested[3b,5] that this is due to the polar character of the homolytic scission transition state **2**.[7b] Formation of such a transition state should lead to an increase in solvent organization over that for the reactant. Such a process would be facilitated by pressure ($\Delta V^*_{solv} < 0$) and might be expected to partially compensate for the positive activation volume associated with bond stretching.[9]



2

We now report the effect of ring substitution on the pressure dependence of the decomposition rates of *tert*-butyl phenylperacetate. The data are in agreement with the general conclusions previously outlined for the unsubstituted perester.[3b] Additionally they suggest that transition state polarity **2** varies with substituent, and they also provide a basis for explaining the pressure dependence of the observed activation volumes.

(1) (a) Part V: R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970). (b) Support by the National Science Foundation (GP-4287, 7349, and 8670) is gratefully acknowledged.

(2) Taken from the Ph.D Dissertation of J. V. Behar, University of California, Riverside, 1969.

(3) (a) Activation volumes are related to the pressure dependence of reaction rate constants according to the equation $\partial \ln k/\partial P = -\Delta V^*/RT$. A detailed list of reviews has been presented.[3b] (b) See R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969).

(4) For the general scheme for homolytic scission reactions, the observed

$$\text{initiator} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{geminate radicals} \xrightarrow{k_d} \text{free radicals}$$

decomposition rate constant is given by the equation $k_{obsd} = k_1/(1 + k_{-1}/k_d)$. The quantity $k_{obsd} = k_1$ (and $\Delta V^*_{obsd} = \Delta V^*_1$) only when the geminate radicals cannot recombine to regenerate initiator ($k_{-1} = 0$).[1a,3b]

(5) (a) R. C. Neuman, Jr., and J. V. Behar, *Tetrahedron Lett.*, 3281 (1968); (b) *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

(6) A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1956).

(7) (a) On the basis of kinetic and product data for these[7b] and other peresters,[7c] Bartlett concluded that the peresters **1** decompose by simultaneous two-bond scission (eq 2). (b) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960). (c) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

(8) For leading references to Bartlett's studies of peresters, see J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

(9) (a) Activation volumes expected for solvation or solvent electrostriction are reviewed by W. J. LeNoble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967); (b) see also M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 375 (1935).