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Reaction of 4*a*,10*a*-Bromomethano-1,1-dimethyl-9-oxo-1,2,3,4-tetrahydrophenanthrene with Nucleophiles

We have previously reported[1] a new method for angular formylation[2] by the solvolytic ring opening of bromocyclopropyl compounds.[3] We now wish to report that a bromocyclopropyl group is converted into angular nitromethyl, cyanomethyl, and sulfonylmethyl group by the reaction with sodium nitrate, potatium cyanide, and sodium *p*-toluenesulfinate, respectively.

4*a*,10*a*-Bromomethano-1,1-dimethyl-9-oxo-1,2,3,4-tetrahydrophenanthrene (I) was prepared as mentioned before[1] and its reaction with several nucleophiles was divided into the three following types.

Type 1: Displacement of bromine on the cyclopropane ring and spontaneous ring opening to form 4*a*-substituted methyl groups.

Type 2: Substitution of bromine without ring opening.

Type 3: Substitution of bromine and spontaneous ring opening to form 10*a*-substituted compounds.

None of the nucleophilic reagents used afforded products other than those formed by these three types of reactions.

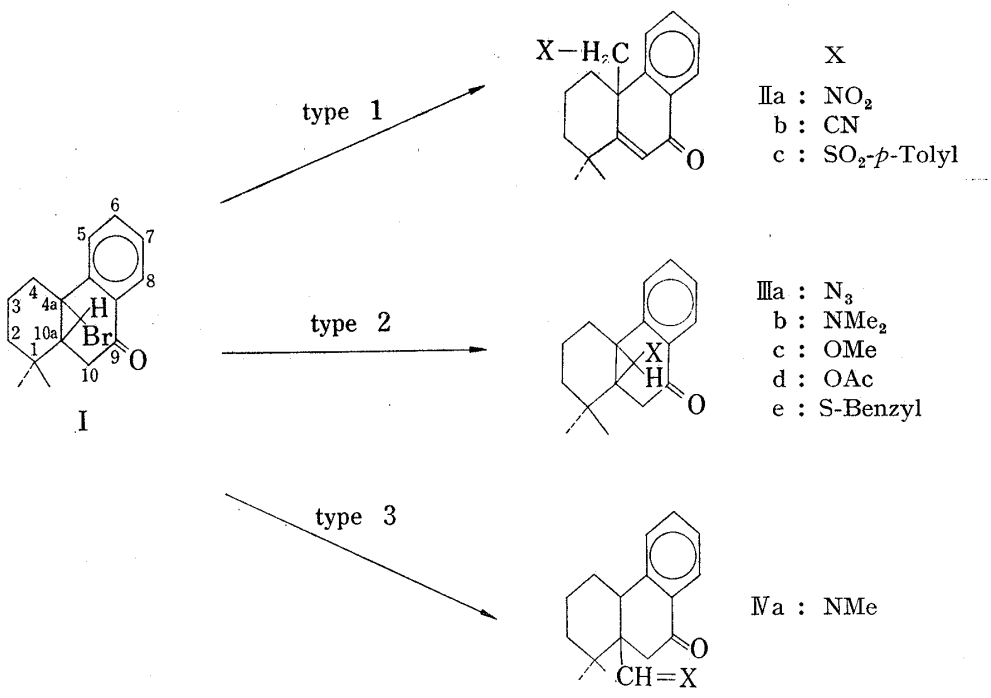


Chart 1

The reaction conditions are summarized in Table I. The structures of the products are confirmed by satisfactory elemental analyses, and from infrared (IR) and nuclear magnetic resonance (NMR) spectra. The data for the products are summarized in Table II. The IR spectra (KBr) of IIa, IIb, and IIc showed absorptions at 1650 cm^{-1} (α,β-unsaturated

1) H. Yamaguchi, T. Maeda and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 1145 (1968).
2) Angular alkylations via cyclopropane ring openings. *a*) J.J. Sims, *J. Org. Chem.*, **32**, 1751 (1967); *b*) H.O. Hause and C.J. Blankley, *J. Org. Chem.*, **33**, 47 (1968); *c*) E. Wenkert and D.A. Berges, *J. Am. Chem. Soc.*, **89**, 2507 (1967).
3) J.A. Landgrebe and L.W. Becker, *J. Am. Chem. Soc.*, **89**, 2506 (1967).

carbonyl group) and at 1545 cm^{-1} (NO_2) 2240 cm^{-1} (CN), and 1332 cm^{-1} (SO_2) respectively. The NMR spectra exhibited olefinic protons at 3.3—3.4 τ (1H, singlet, C-10) and substituted methyl protons as an AB-pattern quartet (2H, J=11, 16 and 15 cps respectively $-CH_2X$ attached to C-4a).

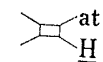
The presence of cyclopropane ring in IIIa, IIIb, IIIc, IIId, and IIIe was confirmed by NMR spectra which showed singlets assigned for protons on the substituted cyclopropane ring at 6.67, 8.06, 6.72, 5.30, and 7.57 τ, and AB-pattern quartets assigned for C-10 methylenes. The substitutents on the cyclopropane ring of IIIb, IIIc, IIId, and IIIe could be oriented to the aromatic ring because the observation of unusual high field shifts of the substituents could be explained by anisotropy effect of the aromatic ring; IIIb 8.23 τ (▷— $N(CH_3)_2$), IIIc 7.34 τ (▷— O–CH_3), IIId 8.42 τ (▷— OCO–CH_3), and IIIe 7.00 τ (▷— S–CH_2Bz). The structure and stereochemistry of IVa were described previously.[1]

Table I. Conditions for I with Several Nucleophiles

Reaction type	Reagent	Solvent	Temperature (°C)	Product	Yield (%)
1	$NaNO_2$	DMSO	50—60	IIa	50
	KCN	DMSO	60—80	IIb	70
	$NaSO_2$-Ar[a]	DMSO	50—60	IIc	88
2	NaN_3	DMSO	45—60	IIIa	80
	Me_2NH	EtOH	140—150	IIIb	95
	MeOH	MeOH	120—150	IIIc	75
	AgOAc	AcOH	25	IIId	7
	NaS-Bz	DMSO	25	IIIe	100
3	$MeNH_2$	EtOH	150	IVa	69

a) Ar=*p*-Tolyl

Table II. IR and NMR Data of Reaction Products

Compound			IR ν_{max}^{KBr}		NMR (τ) (in $CDCl_3$ at 23°)	
	X	mp[a]		$-CH_2-X$	 at C_{10}	$-CH_2-X$ (J, cps)
IIa	NO_2	174—175	1650	1545	3.32	5.17 5.03 (J=17)
IIb	CN	204.5—205.5	1650	2240	3.40	7.16 6.92 (J=16)
IIc	SO_2tolyl	234—235	1650	1332	3.32	6.32 5.78 (J=15)
						$-CH_2$ -at C_{10} (J, cps)
IIIa	N_3	102—103	1670	2090	6.67	7.40 7.14 (J=17)
IIIb[b]	NMe_2	111—112	1675	—	8.06	7.77 7.20 (J=17)
IIIc	OMe	120—121	1685	1295	6.72	7.52 7.16 (J=17)
IIId[c]	OAc	oil	1685	1750	5.30	7.32 7.03 (J=17)
IIIe	SBz	81.5—82.0	1685	1455	7.57	7.55 7.35 (J=16.5)

a) uncorrected b) NMR at 70° c) IR ν_{max}^{cap} cm^{-1}

The separation into these three reaction types could be ascribed to the attacking nucleophiles.

Type 1: The possible mechanism of this reaction type involves the substituted cyclopropyl intermediate (V). With substituents such as nitro, cyano, and sulfonyl groups, V should be converted into an anionic intermediate (VI) with spontaneous ring opening from the bond A because of stabilization by the substituents.[4]

Type 2: Substituted cyclopropane ring does not open when the substituents were dimethylamino, methoxy, acetoxy, or thiobenzyloxy groups.

Type 3: The cyclopropyl intermediate (V) should be present.

By the removal of an active proton from the substituents such as methylamino or hydroxyl group,[1] V should be converted into the most stable anionic intermediate[5] (VII) with the ring opening from the bond B.

Further studies on the ring opening reaction of the substituted cyclopropane are now in progress.

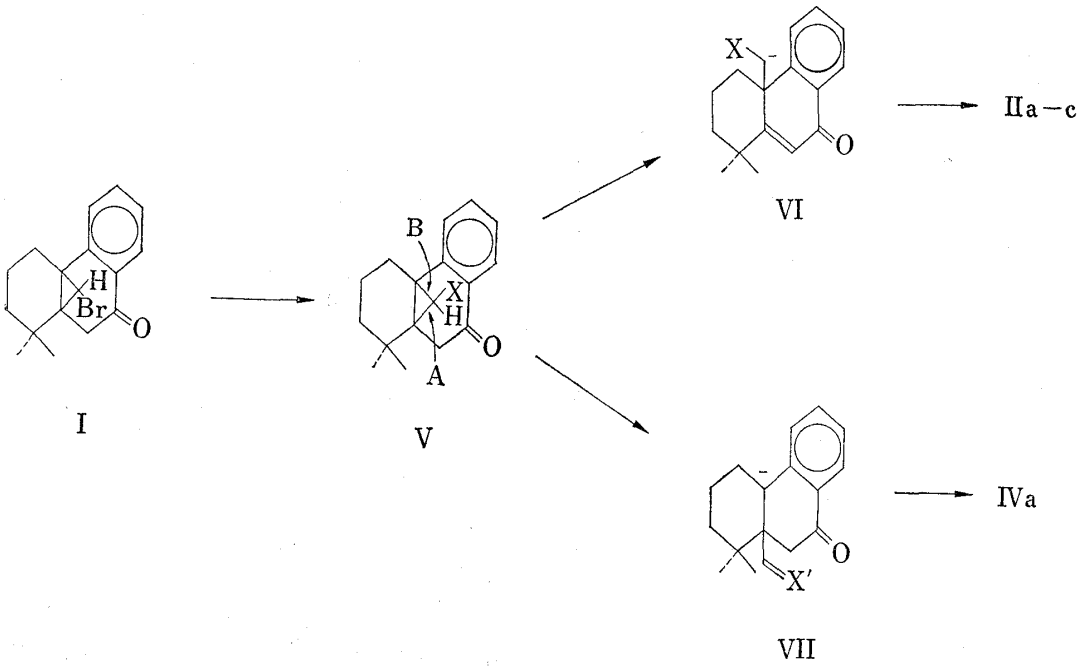


Chart 2

Faculty of Pharmaceutical Sciences,
University of Tokyo,
Hongo, Bunkyo-ku, Tokyo

Hisao Yamaguchi
Toshihiko Okamoto

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4) D.J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, Inc., London and New York, 1965.
5) C.H. DePuy, F.W. Breitbeil, and K.R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966).